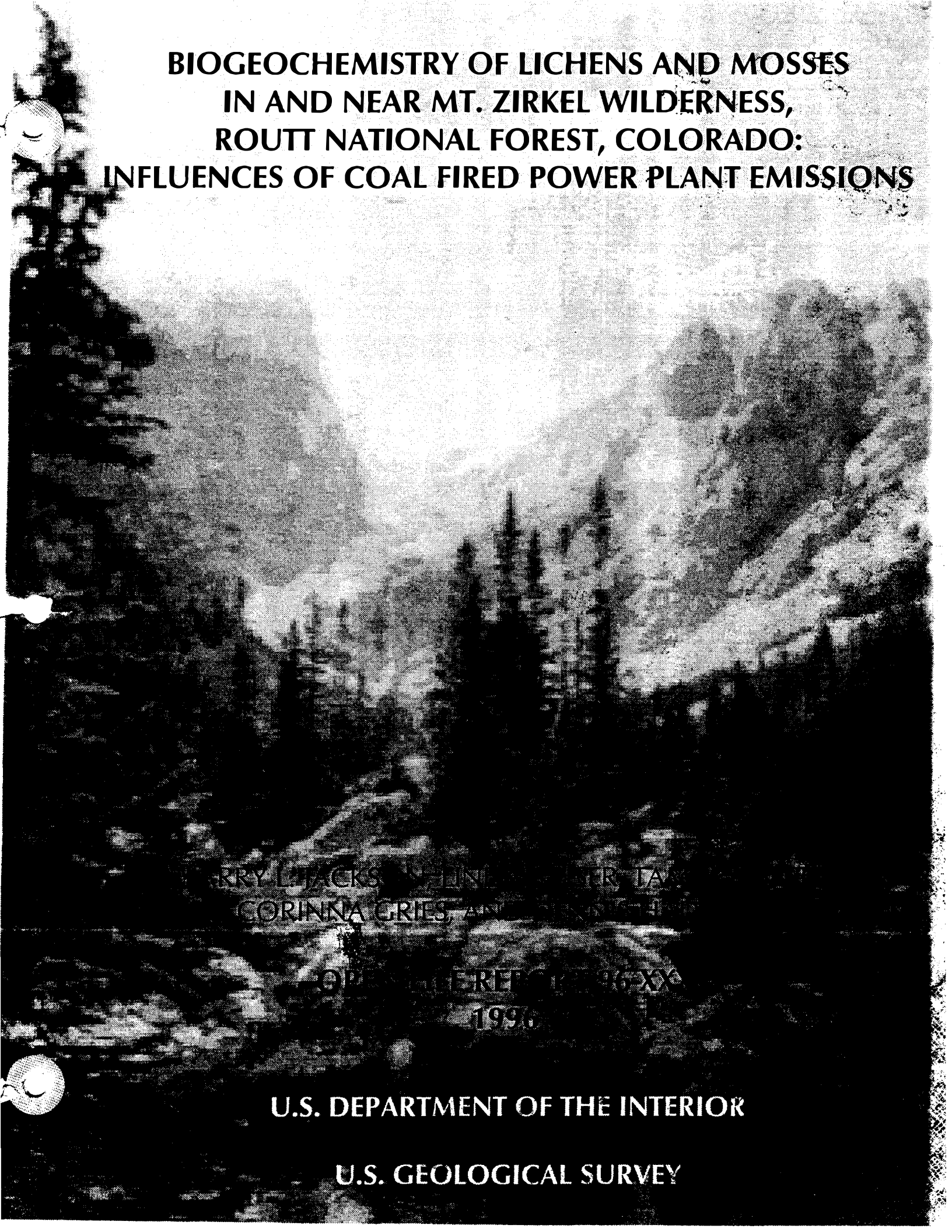
BIOGEOCHEMISTRY OF LICHENS AND MOSSES IN AND NEAR MT. ZIRKEL WILDERNESS, ROUTT NATIONAL FOREST, COLORADO: INFLUENCES OF COAL FIRED POWER PLANT EMISSIONS



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Biogeochemistry of Lichens and Mosses in and near Mt. Zirkel Wilderness, Routt National Forest, Colorado: Influences of Coal-Fired Power Plant Emissions

by

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EXECUTIVE SUMMARY

Biogeochemistry of Lichens and Mosses in and near Mt. Zirkel Wilderness, Routt National Forest, Colorado: Influences of Coal-Fired Power Plant Emissions

This report presents the methods, chemical and physiological analysis results, and conclusions of a study of lichen chemistry in the subalpine zone of Mt. Zirkel Wilderness (MZW) and other wilderness areas in northern Colorado and lichen and moss chemistry in the Yampa Valley. This study was conducted by the U. S. Forest Service (USFS), with assistance from the U. S. Geological Survey (USGS), to assess the potential influence of two coal-fired power stations in the Yampa Valley upon terrestrial ecosystems in the Class I air quality region of MZW. The USFS has indicated that, based on the information available, it is reasonable to suspect that the upwind coal-fired power plants at Craig and Hayden, which are the greatest point sources of SO_2, NO_x, and particulates in northwest Colorado, are contributors to some degree to the impairment of visibility and air-quality-related values in the MZW. The current status and potential pollution impacts on terrestrial components of MZW ecosystems are not known. Lichens and mosses are well known as sensitive indicators of atmospheric deposition in terrestrial ecosystems and we are using them to begin to assess atmospheric emission influences on MZW terrestrial air-quality-related values.

Lichens were collected in the subalpine zone of MZW and regional sites in other national forest lands within northwest Colorado and southern Wyoming, and the east-west trending portion of the Yampa River Valley. Moss was also collected within the Yampa Valley. Major and trace element concentrations were determined on all lichen and moss samples. Stable sulfur isotope ratios were determined on a subset of lichen and moss samples. Several physiological analyses such as chlorophyll content and degradation and photosynthesis rate were performed in the laboratory on some species.

Lichens (*Bryoria fuscescens*, *Usnea lapponica*, and *Xanthoparmelia cumberlandia*) were collected in the subalpine zone in the wilderness areas. Collections were made of the lichen *Xanthoria* spp. from the Yampa River riparian zone and the moss *Tortula ruralis* from the sagebrush zone within the Yampa Valley.

Coal-fired power plants emit a variety of metals and metalloids along with nitrogen and sulfur gases. Many of the elements are phytotoxic and may be enriched in lichens and mosses in the vicinity of a power plant. By measuring major and trace element concentrations in lichens and mosses, enrichment of elements can be estimated, and the spatial distribution of elements around a point source of emissions can be assessed. For sites that were less than 60 km from the Hayden Power Station (i.e., sites within MZW and Routt National Forest), nitrogen, sulfur, potassium, sodium, and phosphorous concentrations were significantly higher ($p < 0.05$) in the lichen *Xanthoparmelia* than at regional sites more than 100 km away. Concentrations of boron, an element commonly emitted by coal combustion processes, were also significantly higher ($p < 0.05$) in *Bryoria* at MZW and nearby sites compared to more distant regional sites.

Coal-fired power plants typically emit sulfur dioxide with a stable isotopic ratio ($^{34}S/^{32}S$) that is characteristic of the coal combusted. Previous studies of lake and snow

chemistry have found a relatively heavy sulfur isotopic ratio (i.e., more positive) at sites in and near MZW, whereas the sulfur isotope ratios were lighter in areas that were either more distant or not downwind of the Yampa Valley power stations. Stable S isotope ratios in the lichen *Usnea* were significantly heavier ($p < 0.05$) in MZW and nearby sites compared to more distant regional sites. In the vicinity of Buffalo Pass, the stable sulfur isotope ratio in *Usnea* is heaviest (forming a distinct maximum) for the north-south trending sites within MZW and southern Routt National Forest. Stable sulfur isotope ratios are typically +7‰ or heavier in snow in the MZW and southern Routt National Forest, particularly in the vicinity of Buffalo and Rabbit Ears Passes. These are also the sites that are closest to the power stations and directly downwind. The heavy S isotopic signature found in the *Usnea* tissue in this study (average $+7.2 \pm 0.7$‰ for sites < 60 km from Hayden station) corresponds well with the sulfur isotopic ratios found in snow in earlier studies at the same area. The isotopic ratios in *Usnea* in MZW and Routt National Forest were significantly heavier than at regional sites (average $+6.0 \pm 0.6$‰) and are consistent with a local sulfur source with a heavy isotopic signature such as would derive from the combustion of many of the marine-influenced coals in the Yampa Valley. Stable S isotope ratios that averaged +6.6, $+8.8 \pm 2.2$‰, and $+8.9 \pm 0.8$‰ have been measured by other groups in Wadge coal from several mines in the Yampa Valley. We found an average value of $+9.9 \pm 0.5$% for Wadge coal from the Seneca 2 Mine, the mine producing coal for the Hayden Power Station. A lighter isotopic ratio (+5.4‰) was found for a single coal sample from the Q seam in the Trapper Mine, one of many seams used in the Craig Power Station. Future research needs to include isotopic analyses of the coals combusted and power station emissions over time in order to fully understand the implications of the stable sulfur isotopic ratios in the lichens.

Potential impacts on physiological functions of the lichens and moss from power station emissions are not obvious outside of the Yampa River Valley in this study. The chemical data show clearly that the deposition is elevated and accumulation in the environment is highly possible. It is not clear yet, when these accumulations may reach a threshold level for the lichens to become damaged or for us to detect such damage. Local variability in canopy, substrate, topography, lichen age, and a variety of other factors may have obscured any detectable trends for these physiological parameters that have most frequently been tested in controlled laboratory fumigation studies.

Although not all lichen species exhibited the same element concentration trends, the aggregate of trends in elevated concentration of elements such as nitrogen, sulfur, and boron in lichens in and near MZW and the corresponding heavy stable sulfur isotope ratios in the lichens and snow strongly suggest a local atmospheric source. Because the Yampa Valley power stations are the predominant source of nitrogen and sulfur emissions upwind of MZW and the limited analysis of coal from the region suggests that the sulfur isotopic signature of the power plant emissions are likely to be similar to that measured in MZW lichens and snow, it is reasonable to assume that the power stations are contributing to atmospheric deposition of nitrogen and sulfur and probably some other elements in MZW. In addition, it appears that sites in the southern portion of MZW and immediately to the south in Routt National Forest that have particularly high precipitation largely in the form of snow and are closest to the upwind power stations are most likely to be impacted by atmospheric deposition.

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Additional lichen samples (*Xanthoparmelia cumberlandia*) were collected in Routt National Forest and at several regional sites in the summer of 1993 by Steve Sharnoff for the U.S. Forest Service. The samples were analyzed by the U.S. Geological Survey through the auspices of Larry Gough. The unedited results are included in this report. Stephen Sharnoff and Sylvia Duran Sharnoff have graciously granted permission to reproduce several of their lichen photographs in this report.

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CONVERSION FACTORS

Measurement values in the International (metric) System (meter/kilogram units) used in this report may be converted to the U.S. Customary System (inches/pounds units) by using the following factors:

To convert from	To	Multiply by
millimeter (mm)	inch (in)	0.03937
meter (m)	foot (ft)	3.281
	yard (yd)	1.094
kilometer (km)	mile (mi)	0.6214
hectare (ha)	acre	2.471
kilometer^2 (km^2)	mile^2 (mi^2)	0.3861
gram (g)	ounce avoirdupois (oz avdp)	0.03527
kilogram (kg)	pound avoirdupois (lb avdp)	2.205
liter (l)	quart (qt)	1.057

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INTRODUCTION

Study Objectives

The primary objective of this study was to assess some of the chemical and biological effects that coal combustion emissions may have on selected non-vascular vegetation (lichens and moss) in and near Mount Zirkel Wilderness. These effects included examining elevated or decreased element concentrations due to increased atmospheric exposure to contaminants or acid precipitation, and deleterious influences on physiological functions such as photosynthesis and chlorophyll content. The biogeochemical data for lichens and moss that were collected are to provide an important baseline against which future changes can be monitored.

Overview of Mt. Zirkel Wilderness Air Quality Related Issues

Mt. Zirkel Wilderness (MZW) is composed of 56,600 hectares (140,000 acres) along the Continental Divide in Routt National Forest in northwest Colorado (Figure 1). The wilderness has been designated as a Class I air-quality region under the Federal Clean Air Act, and as such must receive the highest level of protection from air pollution impacts. "Impact" as used in this report is defined as "human-caused change" in the biological, physical, or chemical character of an ecosystem or plant community. Impact of pollutants on vegetation is often first observed as visible symptoms of plant injury (e.g., chlorosis or necrosis) or by chemical analysis of plant tissue. Chemical analysis of plant tissue is especially useful because it can show bioaccumulation of major and trace elements before more serious pollutant-caused change in reproduction, growth, and mortality occurs in the plant community.

As the federal land manager, the U. S. Forest Service (USFS) has "an affirmative responsibility to protect air-quality-related values including visibility from adverse impacts from air pollution." The MZW contains spectacular scenery and complex aquatic and terrestrial ecosystems. Many lakes within MZW have naturally extremely low alkalinities which make them sensitive to even small additions of acidic substances such as sulfates and nitrates. Snow chemistry data have revealed that snowpack along the Continental Divide downwind of the Yampa Valley contains approximately twice the concentration of sulfate and nitrate and approximately two and one half times the snowpack acidity of other high elevation sites in Colorado (Ely and others, 1993; Turk and others, 1992). The area receives more precipitation than any other area in the State, greater than 1.5 m per year, mostly in the form of snow. Monitored loadings (total wet deposition) of sulfate and nitrate in precipitation are more than twice those in the rest of the State.

Photographic data indicate that there is elevated haze, ground based layered haze, and local visibility impairment within MZW. The photographic record of the layered hazes provides reasonable visual evidence that an individual or small group of sources are causing or contributing to a portion of the visibility impairment within the wilderness. This impairment is distinct from regional haze (haze covering a large geographical area from a

NORTHWEST COLORADO

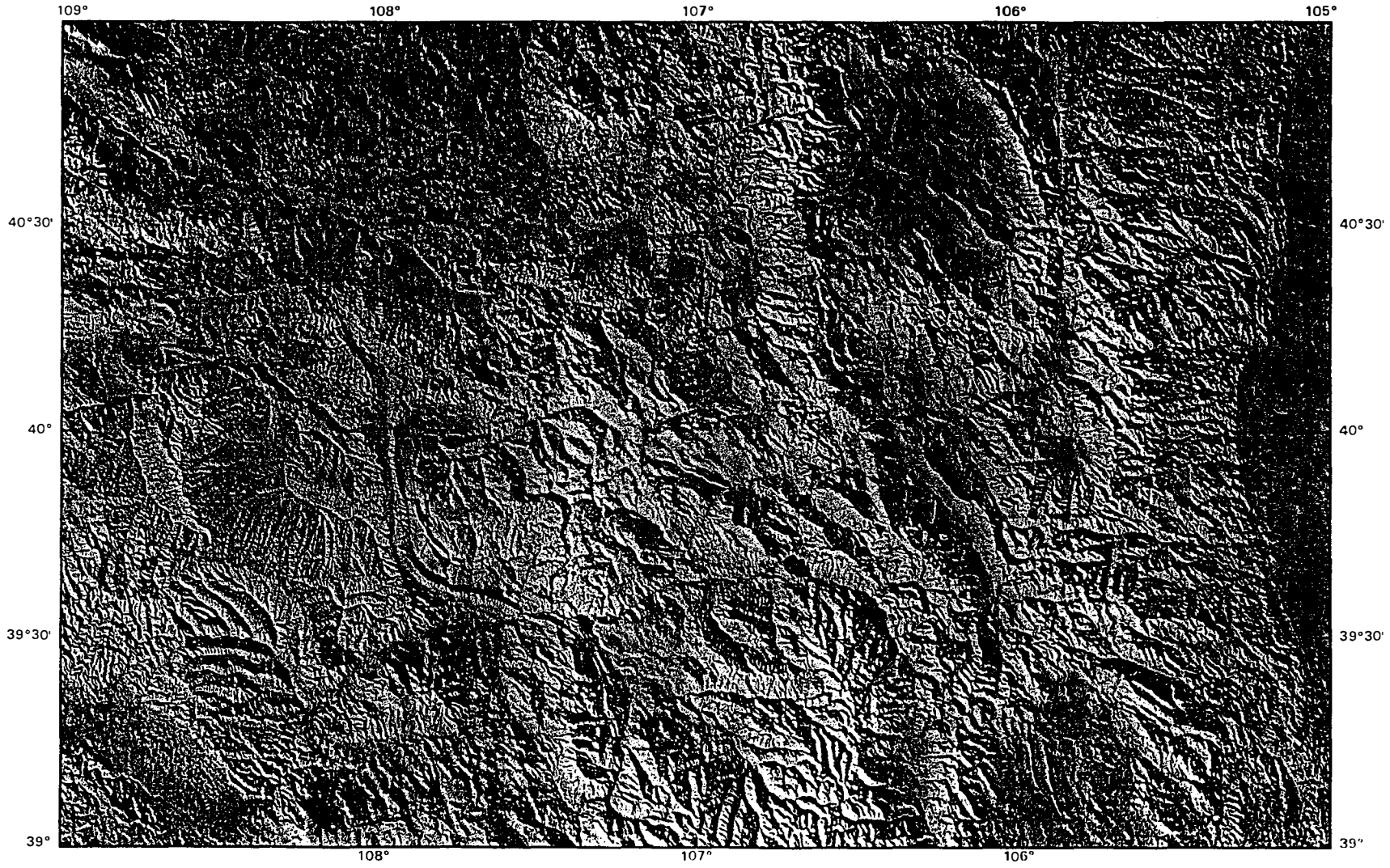

Figure 1. Shaded-relief map of Northwest Colorado.

multitude of sources, often transported large distances) which may also be causing a portion of the visibility impairment within the wilderness.

In July, 1993 the Forest Service sent a letter and supporting technical documentation to the Governor of Colorado formally certifying impairment of visibility and aquatic ecosystems in MZW (Estill, 1993; Ely and others, 1993). The USFS has indicated that, based on the information available, it is reasonable to suspect that the coal-fired power plants at Craig and Hayden, Colorado, are contributors to some degree to the impairment of visibility and air-quality-related values in the wilderness. The current status and potential pollution impacts on terrestrial components of MZW ecosystems are not known. To begin to assess potential coal combustion emission influences on MZW terrestrial air-quality-related values, we have studied the biogeochemistry of lichens and mosses in and near MZW. Lichens and mosses are well known as sensitive indicators of atmospheric deposition in terrestrial ecosystems (Nash and Gries, 1991; Richardson, 1992).

The power plants in the Yampa Valley at Craig and Hayden are located 68 km (42 mi) and 34 km (21 mi), respectively, upwind from the MZW. The prevailing winds in the area are from west to east (Knopf and Borys, 1993; Lewis and others, 1984) and based on preliminary computer modeling of meteorological and emissions data the power plants are implicated as potential contributors to visibility impairment in the MZW. The power plants which together emit more than 22,000 tons[1] of sulfur dioxide, 27,000 tons of nitrogen oxides, and 2,400 tons of particulates are the greatest point sources of these pollutants in northwest Colorado (Ely and others, 1993). Although studies of lake and snow chemistry are highly suggestive that the power plants contribute to higher levels of acidity, studies have not been completed in regard to adverse environmental impacts on terrestrial ecosystems. Biomonitoring is required to assess existing and future impact of pollution sources on sensitive vegetation species within MZW.

Forest Service Air Quality Responsibilities

The Forest Service is charged with the stewardship of all natural resources on National Forests and Grasslands, including the air resource. Stewardship requires that the Forest Service protect the resources they manage from unacceptable air pollution impacts. These requirements stem from several land management acts passed by Congress. The Wilderness Act of 1964 in particular gives the Forest Service the responsibility to manage designated wildernesses to preserve and protect their unspoiled character. It defines Wilderness as "...an area where the earth and its community of life are untrammeled by man.. and ...an area of undeveloped Federal land retaining its primeval character and influence... and ...is protected and managed so as to preserve its natural condition..." In addition to the Wilderness Act, the Code of Federal Regulation for managing Wilderness and Primitive Areas (36CFR 293.2) states "...National Forest Wilderness resources shall be managed to promote, perpetuate, and where necessary, restore the wilderness character of the land..." Also, the National Forest Management Act gives the Forest Service the authority to determine the management goals for Wilderness (which resources should be protected, and

[1]In this report, tons refer to a U.S. short ton (equal to 0.91 metric tons).

to which degree). The Clean Air Act of 1990, as amended, enables the Forest Service to protect air-quality-related values (AQRVs are any wilderness component that can be modified by human-caused air pollution) in Class I areas. Class I areas are wildernesses in existence as of August 7, 1977 exceeding 5,000 acres. Section 165 (d) of the Clean Air Act gives the Forest Service as Federal Land Manager of the Wilderness an affirmative responsibility to protect air-quality-related values including visibility from adverse impacts from air pollution.

Lichens And Mosses As Air Quality Monitors

Lichens are composite organisms of a fungus and a green alga and/~~or a blue-green alga~~ or cyanobacterium. Mosses have small thin green leaves and lack vascular leaf, stem, or root tissues or seeds..Lichens, mosses, fungi, and liverworts comprise a very large group of diverse, often highly evolved, spore producing organisms called non-vascular cryptogams.

Lichens and mosses generally lack mechanisms utilized by higher plants for water uptake (e.g. root systems, conducting tissue) and prevention of gas exchange (e.g. waxy cuticles, stomates). Gas exchange occurs over the entire surface of hydrated lichens and mosses. Elemental content is strongly influenced by the chemistry of the air and precipitation compared to vascular plants. The ability of hydrated mosses and lichens to accumulate sulfur, nitrogen, macro- and trace-elements well beyond their nutritional needs, as well as radionuclides, toxic metals, and semi-volatile hydrocarbons is well documented (Puckett, 1988; Richardson, 1992). Lichens accumulate elements not only by gas exchange but by trapping airborne particulates, by ion-exchange of dissolved metals and other ions to cell walls, and by active transport, particularly of sulfur and phosphorus, across cell membranes (Richardson and Nieboer, 1983; Richardson, 1995). Having little means to control water loss, their hydration state is primarily a function of atmospheric humidity and precipitation. Alternating dry and wet cycles have the effect of concentrating and leaching chemical constituents, influencing the net accumulation of elements from atmospheric and substrate sources. The process is rapid as evidenced by the detection of significant changes in elemental status in seasonal and short term transplant studies (Boonpragob and Nash, 1990a; Gailey and Lloyd, 1986; Garty, 1988).

Owing to their unique biology, lichens and mosses accumulate a wide variety of air pollutants. Tissue concentrations of some elements have been correlated with direct measurements of average annual atmospheric deposition (Herzig and others, 1989; Ross, 1990; Saeki and others, 1977; Sloof, 1995). The measurement of lichen tissue concentrations of sulfur, nitrogen, metals, and other elements reveal relative pollution gradients within the vicinity of a point source, providing a biologically-based receptor method for monitoring air quality (Addison and Puckett, 1980; Baddeley and others, 1994; Burton, 1986; Gough and Erdman, 1977; Nash and Gries, 1991; Nash and Sommerfeld, 1981; Puckett and Finegan, 1980; Richardson, 1992; Sloof and Wolterbeek, 1991; Stolte and others, 1993; Takala and others, 1994; Walther and others, 1990).

Two typical lichen/receptor-based studies have been done around coal-fired power plants in the western United States. Saxicolous lichens growing on sandstone outcrops near the Four Corners Power Plant in New Mexico were analyzed for a variety of elements (Nash and Sommerfeld, 1981). Elevated concentrations of B, F, Li, and Se were observed for

several species within several kilometers of the power plant. Concentrations of Ba, Cu, Mn, and Mo were also elevated, but in only one of the six species sampled. Concentration differences among species were attributed, at least in part, to morphological differences in the lichens. In a similar study in the Powder River Basin, Wyoming, concentrations of Ca, F, Li, Se, Sr, and U and ash content of a foliose lichen decreased with distance from a coal-fired power plant (Gough and Erdman, 1977). The spatial trends and elevated element concentrations in the lichens were attributed to emissions from the power plant. Numerous of the elements that were elevated in the two lichen studies are emitted from coal-fired power plants as volatile species or as reasonably water soluble components of fly ash.

other

Indicators of Coal-fired Power Plant Emissions

The objective in assessing pollutant impact on vegetation or other components of terrestrial ecosystems is to determine whether such impacts exist and, if so, identify the sources of the pollutants and the extent of pollutant impact. In addition to various studies of community structure, physical examination of vegetation for visible symptoms of injury by gaseous pollutants has been used to study the adverse impact of various point and non-point sources of emissions. Although these studies may identify pollution impact, they do not uniquely identify the source of a pollutant.

One physicochemical method that has been used for source identification is the visual and chemical microscopic examination of vegetation surfaces for identifiable pollutant particulates such as the high-iron microspheres produced by high temperature combustion in coal-fired power plants (Gough and Erdman, 1977; Olmez and others, 1985). The presence of fly-ash microspheres on leaf or lichen thalli surfaces would provide clear evidence that power plant particulate emissions are present and contacting vegetation. It is important to note that their presence or absence is a separate question from whether or not there is an adverse impact to vegetation, or other components of terrestrial ecosystems, from these or other emissions.

Various chemical techniques have been widely used for biomonitoring of impact of pollutant sources. Receptor-based studies, such as biomonitoring, typically use total chemical analysis of vegetation to determine enrichment factors, multivariate interelement relationships, element concentration-distance trends, and stable isotope ratios that can be associated with anthropogenic and natural emissions sources. Receptor-based models suffer from the difficulties inherent in identifying contributions from multiple sources at a receptor site. However, because coal and the resulting power plant emissions often have specific chemical signatures, it is sometimes possible to uniquely identify a pollutant source and to apportion the amount of pollutants received from a number of pollutant sources.

In this study four receptor-based measurement types were used to examine potential pollutant emission impacts on MZW. The most traditional measurement type was the determination of major and trace[2] elements in lichens and moss to look for element enrichment and dispersion patterns in and near MZW. A second measurement type used

[2]Major and trace elements are those elements commonly found at percent and $\mu g/g$ concentration levels, respectively.

stable S isotope ratios to look for unique combustion-emission signatures. The third was the determination of lead isotope ratios in a very small subset of samples to examine the feasibility of using lead isotope ratios as an emissions signature. The determination of lead isotope ratios is much less common than the use of S isotope ratios in this type of study. The fourth measurement type was to examine various physiological parameters particularly related to pollutant sensitive photosynthesis processes. This fourth approach was exploratory in that it has not generally been used in large field studies, but has more commonly been used in laboratory fumigation studies and field studies involving transplants of sensitive lichen species.

Coal-fired power plants typically emit sulfur dioxide with a stable isotopic ratio ($^{34}S/^{32}S$) that is characteristic of the coal combusted and that is not fractionated significantly during atmospheric transport (Newman and others, 1975). Turk and others (1993) have measured stable sulfur isotope ratios in lakes and snowpack that ranged from +5.0 to +8.4‰ (per mil) at sites in the MZW and surrounding region. Snowfall at Rabbit Ears Pass near MZW was at the high end of the range compared to surrounding areas which were either more distant or not downwind of the Yampa Valley power plants. Krouse (1977) and Case and Krouse (1980) have shown that lichens have sulfur isotopic signatures similar to ambient air sulfur and characteristic of specific pollutant emission sources. Nriagu and Glooschenko (1992) have used stable sulfur isotope ratios as tracers of sulfur sources in regional studies in Canada. Thus, sulfur isotope signatures of MZW lichens and mosses, which take up sulfur directly from the atmosphere, may provide direct evidence of the presence of power plant sulfur-related emissions on vegetation in MZW, corroborating evidence from lake and snowpack studies.

Ratios of lead isotopes in lichens also offer the potential for unique identifiers of pollutant sources. Church (1993) has used the ratios of $^{208}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ to conclusively identify the source of lead in stream sediments in the Leadville mining district. Similar techniques have been used by Jaakkola and others (1983) to estimate the relative contribution from gasoline and incinerator ash to lead in lichens. The lead isotopic ratios in epiphytic lichens have been used in the boreal forests in southern Quebec, Canada to identify significant input of anthropogenic lead from smelting activities in lichens up to 500 km from the smelter (Carignan and Gariepy, 1995).

Coal-fired power plants emit a variety of metals, metalloids, and non-metals as solid phase particles of varying size in addition to gas phase emissions of some volatile elements (Davison and others, 1974; Eary and others, 1990; Kaakinen and others, 1975; Klein and others, 1975a,b; Mattigod and others, 1990; Ondov and others, 1979; Warren and Dudas, 1989). Fly ash is predominantly an aluminosilicate glass with various crystalline materials including magnetic iron oxides (Mattigod and others, 1990; Querol and others, 1993; Warren and Dudas, 1989). In addition to the major element emissions such as S and N, coal combustion is a major source of atmospheric beryllium (Lee and Daffield, 1979) and boron (Anderson and others, 1994; Fogg and Rahn, 1984; Gladney and others, 1978) along with other elements that are emitted including antimony, arsenic, cadmium, chromium, lead, magnesium, manganese, mercury, nickel, selenium, thallium, titanium, vanadium, and zinc. During combustion, these elements may partition among different phases such as bottom ash, fly ash, and combustion gases. The volatile trace elements, B, Hg, Se, and halogens, are

commonly enriched in the gas phase emissions, although B and Se may also behave similarly to As, Cd, Ga, Ge, Pb, Sb, Sn, Te, Tl, and Zn by being volatilized during combustion and then condensing on the smaller combustion particles in the flue gases (Clarke, 1995). Barium, Be, Bi, Co, Cr, Cs, Cu, Mo, Ni, Sr, Ta, U, V, and W may also go through the volatilization-condensation process. However, these latter elements may also concentrated in coarse particulates similarly to Eu, Hf, La, Mn, Rb, Sc, Sm, Th, and Zr (Clarke, 1995). Many of the elements are phytotoxic depending upon their form and may be enriched in vegetation and soils in the vicinity of a power plant. Trace elements that have been of greatest concern are As, B, Cd, Pb, Hg, Mo, and Se, whereas elements of moderate concern include Cr, V, Cu, Zn, Ni, and F (National Research Council, 1980). By measuring trace element concentrations in lichens and mosses, element enrichment can be estimated and the spatial distribution of elements around a point source can be assessed. These trace element concentration measurements also provide a reference point or baseline measurement against which future changes may be assessed.

In addition to measurement of trace element concentrations, a number of biochemical parameters can be measured to examine impact from various pollutants. Anthropogenic emissions are believed to adversely affect photosynthesis and chlorophyll content of lichens. The measurement of these biochemical parameters in lichens with respect to distance from a power plant offers a unique way to directly examine the potential adverse impact of emissions on critical biological functions.

Environmental Setting

Mt. Zirkel Wilderness straddles the Continental Divide along the north-south trending Park Range in Routt National Forest from about the Colorado-Wyoming border southward to Buffalo Pass (Figures 1 and 2). Elevations range from about 2,400 m (8,000 ft) to more than 3,600 m (12,000 ft). The Sierra Madre Range is the northern extension of the Park Range and the Gore Range extends to the south. MZW is underlain by metavolcanic and metasedimentary rocks of Precambrian Age with many areas covered by Quaternary glacial tills and alluvial gravels (Snyder, 1980a,b,c; Snyder and others, 1987). The latter tills and gravels are especially prominent in the glaciated, more rounded terrain along the Continental Divide from Buffalo Pass to Rabbit Ears Pass where the maximum elevations are generally 3,200 m (10,400 ft) or less. The most rugged, high elevation (3,600 m) areas are in the central portion of MZW from Mt. Ethel and Lost Ranger Peak, where the quartz monzonites of the Mt. Ethel pluton are exposed, northward to Mt. Zirkel and Big Agnes Peak, where metavolcanic gneiss and older quartz monzonites predominate. These latter Precambrian rocks are also dominant in the northernmost section of MZW along with Quaternary tills on many slopes and in drainages such as Encampment River.

MZW generally has the highest annual average precipitation within Colorado with most of the 100 to more than 150 cm of precipitation in the form of snow (Doesken and others, 1984). The highest precipitation is in the southern portion of MZW from Mt. Ethel to Buffalo Pass. The heavy snowfall causes abundant spring runoff typically beginning in April to early May. The eastward drainage of MZW flows into North Park and the Platte River system and westward drainage flows into the Elk and Yampa Rivers.

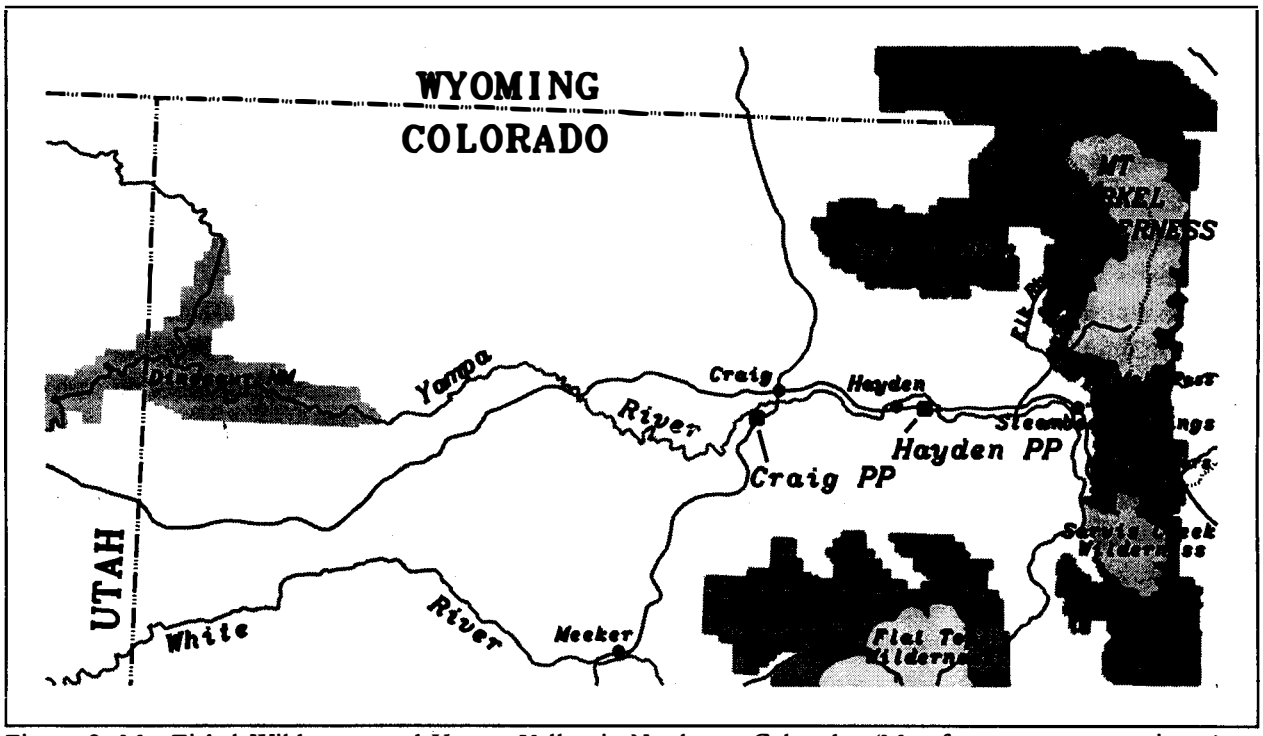

Figure 2. Mt. Zirkel Wilderness and Yampa Valley in Northwest Colorado. (Map features are approximate)

In water year[3] 1993, four SNOTEL sites in Routt National Forest indicated that they received precipitation predominantly from the west and north-west (Knopf and Borys, 1993). In a hydrochemical study of a small subalpine catchment near Rabbit Ears Pass (Peters and Leavesley, 1995), storms were largely from the southwest. Within the catchment, average daily maximum temperatures ranged from about -4°C to 20°C, winter to summer, and average daily minimum temperatures ranged from about -17°C to 8°C, winter to summer.

Vegetation zones within the wilderness include the upper montane with lodgepole pine and aspen, the subalpine with Engelmann spruce, subalpine fir and aspen, and the alpine which is dominated by grasses, forbs, and shrubs, and scattered krummholz of spruce or fir. The subalpine zone is typically found at elevations from 2,600 m to treeline at 3,200-3,500 m (USDA-Forest Service, 1983). Soils are generally classified at the Great Group level as Cryoboralfs-Cryoborolls that are less developed, rocky upland slope soils formed from glacial till, weathered bedrock, and eolian dust (Driver and others, 1984, Snyder and others, 1987).

The Yampa River flows westward from Steamboat Springs through Craig to join the Green River in Dinosaur National Monument at the Colorado-Utah border. The Yampa

[3]In this report, water year generally refers to precipitation during the period of October 1 of the previous year to September 30 of the listed year (e.g., water year 1993 is October 1992 through September 1993).

Valley is bounded on the south by the high elevation (2,600-3,600 m) White River Plateau and the lower elevation Williams Fork Mountains and the Danforth Hills. The northeastern portion of the valley is bounded by the Elkhead Mountains. The Uinta Mountains are at the western edge of the Yampa River Basin. Elevations within the valley range from about 1,800 to 2,400 m.

The Yampa Valley is dominated by sedimentary strata of shales and sandstones, with varying degrees of marine influence, from the Cretaceous and Tertiary Periods (BLM, 1980; Driver and others, 1984). Extensive coal beds are found within the Iles and Williams Fork Formations in the Mesaverde Group of Late Cretaceous Age. Slightly younger coals are found in the Late Cretaceous Lance and Tertiary Fort Union Formations. The coals are primarily bituminous in rank, although they range from subbituminous to anthracite. The Yampa coal field is a high production area within the Green River Coal Region. In 1990, Routt, Moffat, and Rio Blanco Counties produced more than 75% of the coal mined in Colorado (Maclean Hunter Publishing Co., 1993). Much of the coal mined is referred to as "clean air compliance coal," because it is low in sulfur and ash, and it is used for electrical power generation in and outside Colorado. General stratigraphic columns for the Yampa Valley coal areas are given in BLM (1976), Johnson and Brownfield (1988), and Williams and Clark (1994).

The soils in the valley are classified at the Great Group level as Camborthids, Cryoborolls-Cryothents, Torriorthents, and Haploborolls-Argiborolls formed from residual weathered shales and sandstones, and alluvial and eolian deposits (Driver and others, 1984). Soils are generally loamy in texture with varying amounts of sand and clay depending largely upon the parent material. The soils are generally alkaline and may have high salt concentrations in the subsoil.

Sagebrush with associated grass and forb species dominate the Yampa Valley with riparian zones along the river and some drainages (BLM, 1976). Cottonwood and minor amounts of boxelder, willow, dogwood, and hawthorn are found in the riparian zone. The riparian zone has frequently been grazed or encroached upon by croplands; hay and grains are typical crops. Mountain-shrub and aspen communities are commonly found at higher elevations within the valley.

Precipitation increases eastward within the valley from less than 25 cm yr^{-1} in the semiarid western extremes of the valley up to 60 cm yr^{-1} in the higher elevation eastern areas (Doesken and others, 1984). Local topography strongly influences wind patterns. At the Hayden Power Station, both up and down valley wind patterns are evident (Ely and others, 1993, BLM, 1976). At the Craig Power Station, low altitude winds are frequently from the southwest and west ($\sim$40% of the time; Ely and others, 1993; BLM, 1976). Maximum temperatures vary from about 0°C in winter (January) to 30°C in summer (July) with minimum temperatures of -18°C to 7°C, winter to summer (BLM, 1976). The growing season varies considerably within the valley: 94 days yr^{-1} at Craig, 76 days yr^{-1} at Hayden, and 28 days yr^{-1} at Steamboat Springs (BLM, 1976).

Coal-fired Power Stations and Air Quality in the Region

Mine-mouth, coal-fired power stations are located in the Yampa Valley at Hayden and Craig. The Hayden Power Station Unit 1 has been in operation since 1965 and Unit 2 has operated since 1976. The power station has a nameplate generating capacity of 465 MW (EIA, 1994) with an estimated net load factor of 80%[4] (Maude and others, 1994). The Hayden station burns coal (about 0.44% S and 10.3% ash) and up to 1% oil (Maclean Hunter Publishing Co., 1993). In 1992, bituminous coal consumption was about 1.5 million tons (Maude and others, 1994). Peabody Coal Company has been producing coal from the Seneca and Seneca 2 coal mines for operation of the Hayden station. The Seneca Mine[5] produced about 1.4 million tons in 1992 with about 57% of the coal from the 2.6 m thick Wadge seam and 43% from the 5 m thick Wolf Creek seam. Overall the coal averages 0.4% total S with 0.08% as pyritic S, 0.30% organic S, and 0.02% sulfate S (Maclean Hunter Publishing Co., 1993). Coal production from the Seneca Mine apparently met the demand for the Hayden Power Station. In the past, at least, coal from the high sulfur Lennox seam (1.7% S or greater) was apparently blended with the lower sulfur Wadge seam coal for combustion at the power station (Williams and Hammond, 1988).

The Craig Power Station has three coal-fired units that began operating in 1979, 1980, and 1984 with a combined nameplate generation capacity of 1340 MW (EIA, 1994). The net load factor for continuous full load operation was 63% and in 1992 the power station combusted about 4.5 million tons of subbituminous coal (Maude and others, 1994). The coal has an average S and ash content of 0.37% and 6.87%, respectively. Coal is utilized from the Trapper Mine with an annual production of about 2 million tons of coal that has an estimated overall S content of 0.43%. Numerous coal seams are mined (H: 1.1 m, 10.5% of total; I: 2 m, 42.7% of total; L: 0.9 m, 4.7% of total; Q: 2.8 m, 36.4% of total; and R: 1 m, 5.7% of total)(Maclean Hunter Publishing Co., 1993). Beds H and I are in the middle coal group of the Williams Fork Formation and are slightly higher stratigraphically within the formation as compared to the Wolf Creek and Wadge seams, respectively. Coal beds L through R are in the upper coal group of the same formation. Coal from the Trapper Mine, whose annual production could account for about half of the Craig station's consumption, is apparently used in Units 1 and 2 and additional coal from the Colowyo Mine is apparently consumed in Unit 3 (Hook, BLM, personal communication). We are not aware to what extent coals from these or other mines are blended to meet the combustion needs of the power station.

The chemical characteristics of some of the mined coal seams have been determined by the U.S. Geological Survey and are listed in the Coal Quality Database (Bragg and others, 1994). The limited information available is presented in Table 1 for coal seams within the middle and upper coal groups of the Williams Fork Formation. Although these samples are

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[4]The load factor is the equivalent proportion of a full year of continuous operation.

[5]This information probably pertains to the Seneca 2 Mine, but the Keystone Directory does not distinguish between the mines. The original Seneca Mine is apparently not producing coal in large quantities, if any coal, at this time (Hook, BLM, personal communication).

Table 1. Element concentrations in coal typical of some of the coal used by the Hayden and Craig Power Stations (Bragg et al., 1994).

Coal Seam[1]	LENNOX						WADGE						WOLF CREEK	Q	US avg[2]
Comments[3]		SDH-1	SDH-3	SDH-4	SM	SM	SDH-1	SDH-2	SDH-3	SDH-4	SM	SM2	SM	TM	
Total S%	2.05	2.46	1.92	2.6	2.82	–	0.41	0.39	0.39	0.47	0.42	0.50	0.51	0.26	2.0
Sulfate S%	0.04	0.01	<DL	0.01	0.04	–	<DL	<DL	<DL	<DL	0.01	0.03	0.03	0.03	0.12
Pyrite S%	1.01	1.45	0.78	1.29	1.55	–	0.1	0.08	0.05	0.08	0.09	0.06	0.11	0.04	1.19
Organic S%	0.99	0.99	1.13	1.28	1.23	–	0.3	0.31	0.33	0.37	0.31	0.45	0.37	0.18	0.70
Si, µg/g	16000	6300	9700	8200	13000	6000	17000	9400	15000	19000	15000	26000	23000	4700	26000
Al, µg/g	8300	4300	5600	5300	5500	5400	12000	9600	12000	14000	11000	16000	17000	4300	14000
Ca, µg/g	2900	2500	2800	2800	2500	2500	2200	3000	3000	3000	3500	2600	3300	3900	5400
Mg, µg/g	550	250	370	350	360	300	300	450	400	360	590	580	630	1600	1200
Na, µg/g	550	570	620	780	130	380	1200	710	440	1100	750	340	190	80	600
K, µg/g	240	97	110	210	190	90	330	230	360	480	360	910	330	79	1800
Fe, µg/g	14000	16000	8500	15000	22000	13000	2200	1900	2100	2200	1700	2200	2000	1500	16000
Ti, µg/g	410	190	270	290	320	260	460	340	430	540	400	590	680	160	800
As, µg/g	1.8	3	1.3	7.6	6.1	1.3	1.1	0.57	0.51	0.78	0.39	0.83	1.1	0.51	15
B, µg/g	78	48	41	45	62	53	67	44	54	60	67	73	88	27	50
Ba, µg/g	240	170	180	190	160	120	330	320	220	270	180	180	160	280	150
Be, µg/g	0.95	0.49	0.84	0.36	3.4	0.43	0.97	0.91	0.74	1	0.64	0.86	1.4	0.28	2
Cd, µg/g	0.046	0.031	0.018	0.035	0.034	0.02	0.03	0.02	0.03	0.03	0.02	0.09	0.026	0.01	1.3
Co, µg/g	0.96	0.67	0.58	0.7	0.7	0.86	0.94	0.82	1	1.1	0.86	1.6	1.4	0.74	7
Cr, µg/g	3.8	2.2	2.4	2.9	2.9	2.5	1.6	1.3	1.9	2.7	3.1	1.6	4	1.6	15
Cu, µg/g	8.2	3	4	5.1	6.6	3.5	6.7	6	6	7.2	5.4	6.7	6.8	3.1	19
Hg, µg/g	0.031	0.029	0.025	0.012	0.024	0.15	0.007	0.009	0.006	0.003	0.029	0.035	0.024	0.003	0.18
Li, µg/g	4.7	2.5	3.2	2.7	3.7	3.7	6.9	6.4	8.3	7.7	6.6	10	9.8	1.4	20
Mn, µg/g	12	17	7.6	12	13	9.2	5.1	4.3	4.5	7.5	5.9	7.5	9.3	17	100
Mo, µg/g	0.98	1.7	0.73	1.5	2.6	0.66	1.2	0.58	0.7	1.1	0.44	0.86	0.84	0.75	3
Ni, µg/g	4.5	1.6	1.9	2.4	4	2	4.2	2.2	2.3	3.7	1.9	1.8	3.8	3	15
P, µg/g	220	400	250	180	110	360	430	570	540	380	550	440	300	420	-
Pb, µg/g	3.8	2.5	2.9	3.4	4	9.6	4.6	5.6	4.9	5.7	4.1	5.6	7.1	2.1	16
Sr, µg/g	250	240	240	260	150	230	340	290	250	290	200	90	130	200	100
V, µg/g	9.5	3.9	7.8	5.9	6.9	2.9	7.7	5.2	5.7	8.9	4.4	7.3	9.4	3.6	20
Zn, µg/g	7.3	5.2	2.6	4.9	5.5	6	5.7	3.5	4.5	5.2	3.6	5.4	4.7	3	39

[1]Lennox, Wadge, and Wolf Creek coal seam data are from the Seneca and Seneca 2 Mines (generally, the two mines are not clearly distinguished from each other in the coal quality database) and Q seam data are from the Trapper Mine.
[2]Data for average concentration in U.S. coals are from National Research Council (1980).
[3]Drill cores SDH-1 through SDH-4 are from the Seneca 2 Mine (Brownfield, personal communication), otherwise SM = Seneca Mine, SM2 = Seneca 2 Mine, and TM = Trapper Mine.

from the Seneca and Trapper Mines, it is unknown how representative these data are of the coals combusted by the power stations. As described above, numerous "low sulfur " coal seams are burned at the power stations and depending upon the practices of the mines and the power stations, the chemical characteristics of the coal may be quite variable throughout the year.

As noted above, emissions inventory data indicate that Hayden and Craig Power stations, located immediately upwind of MZW, together emit in excess of 22,000 tons of sulfur dioxide, 2,400 tons of particulates, and 27,000 tons of nitrogen oxides per year (Ely and others, 1993). The power plant emissions represent 99.6% of all sulfur dioxide, 91.1% of all nitrogen oxide and 62.0% of all particulate emissions emitted from stationary sources in Routt, Moffat and Rio Blanco Counties (Ely and others, 1993). Meteorological data indicate that the general prevailing wind direction is from west to east, from the Craig and Hayden Power Stations toward the MZW. Although the available data do not allow a precise quantification of the power stations contributions, photographic, emissions, meteorological, modeling, and sulfur and nitrate deposition data make it reasonable to believe that the Hayden and Craig Power stations are causing or contributing to decreased visibility and impairment of aquatic ecosystems in MZW (Estill, 1993; Ely and others, 1993).

Additional pollution sources in the vicinity of MZW are the Deseret Power Generating Station, approximately 200 km to the west in Bonanza, Utah; and several sources of various pollutant emitting capabilities in southwest Wyoming. In Sweetwater County these include the Jim Bridger Power Plant (also about 200 km from MZW), FMC Trona, General Chemical, SF Phosphates, Sweetwater Resources, Colorado Interstate Gas, Texas Gulf Trona, Solvay Minerals, Union Pacific-Patrick, and Union Pacific-Brady. In Uinta County these include Amoco Whitney Canyon, Chevron Carter Creek, Amoco Anschutz Ranch, Dresser-Rand Company, Universal Resources Corp., Oryx Energy, and Union Pacific-Emigrant. The Naughton Power Station is located in Lincoln County about 350 km to the northwest of MZW. Emissions for the largest regional sources are listed in Table 2.

STUDY DESIGN

Sampling Design

Lichen and moss samples were collected within three spatial units for this study. The spatial areas were the MZW, other wilderness (excluding MZW) and national forest lands within northwest Colorado and southern Wyoming, and the east-west trending section of the Yampa River Valley. Major and trace element concentrations were determined in all lichen and moss samples, whereas stable sulfur isotope ratios were determined in a subset of samples. Several exploratory techniques were used on subsets of selected samples. For example, lead isotope ratios were determined on a small subset of samples and several physiological analyses were performed in the laboratory on some of the species.

Table 2a. Emissions Inventory for SO_2 for selected counties[1] in Colorado, Utah, and Wyoming.

State	County	Facility	Yr	Tons/yr	% tot.[2]	Rank[3]
CO	Routt Co	PUBLIC SERVICE COMPANY - HAYDEN	94	11886	11.8%	2
CO	Moffat Co	TRI-STATE GENERATION - CRAIG	94	10623	10.6%	4
CO	Larimer Co	PLATTE RIVER POWER AUTHORITY	94	867	0.9%	18
CO	Larimer Co	HOLNAM INC.	94	623	0.6%	19
UT	Uintah Co	DESERET GENERATION & TRANSMISSION	90	583	0.7%	11
UT	Duchesne Co	CHEVRON PIPELINE	90	306	0.4%	15
WY	Lincoln Co	PACIFICORP - NAUGHTON POWER PLANT	94	21785	17.3%	2
WY	Sweetwater Co	PACIFICORP - JIM BRIDGER	94	21466	17.0%	3
WY	Uinta Co	AMOCO WHITNEY CANYON	94	5857	4.6%	5
WY	Carbon Co	SINCLAIR OIL CORP	94	5591	4.4%	7
WY	Sweetwater Co	GENERAL CHEMICAL	94	4801	3.8%	8
WY	Sweetwater Co	FMC TRONA	94	4497	3.6%	9
WY	Albany Co	MOUNTAIN CEMENT CO	94	1353	1.1%	14
WY	Sweetwater Co	SF PHOSPHATES, INC	94	1332	1.1%	15
WY	Sweetwater Co	SWEETWATER RESOURCES	94	812	0.6%	23
WY	Sweetwater Co	UNION PAC BRADY	94	334	0.3%	26
WY	Uinta Co	CHEVRON CARTER CREEK	94	297	0.2%	28
WY	Sweetwater Co	TEXAS GULF TRONA	94	222	0.2%	31
WY	Albany Co	UW CENTRL HEAT PLANT	94	221	0.2%	32

Colorado total emissions: 100572 tons

Utah total emissions: 80218 tons

Wyoming total emissions: 126208 tons

[1]Facilities with SO_2 Emissions ≥ 100 TPY (USEPA, 1994, 1995). Counties in the vicinity of the study area and neighboring states.
[2]Percentage of total emissions for the state.
[3]Rank within the state.

Table 2b. Emissions Inventory for NO_2 for selected counties[1] in Colorado, Utah, and Wyoming.

State	County	Facility	Yr	Tons/yr	% tot.[2]	Rank[3]
CO	Moffat Co	TRI-STATE GENERATION - CRAIG	94	17782	13.9%	2
CO	Routt Co	PUBLIC SERVICE COMPANY - HAYDEN	94	10068	7.8%	4
CO	Larimer Co	PLATTE RIVER POWER AUTHORITY	94	3125	2.4%	9
CO	Larimer Co	HOLNAM INC.	94	668	0.5%	25
CO	Rio Blanco Co	CONOCO INC. DRAGON TRAIL GAS PRO.	94	378	0.3%	37
CO	Rio Blanco Co	NORTHWEST PIPELINE CORP. RANGELY	93	357	0.3%	39
CO	Moffat Co	QUESTAR PIPELINE CO. POWDER WASH.	94	270	0.2%	49
CO	Garfield Co	AMERICAN ATLAS NO. 1	93	236	0.2%	56
CO	Garfield Co	ROCKY MTN. NATURAL GAS CO. CRYST.	94	223	0.2%	60
CO	Garfield Co	BARRETT RESOURCES CO. WASATCH YA.	93	184	0.1%	72
CO	Rio Blanco Co	MITCHELL ENERGY CORP - HELLS HOL.	94	167	0.1%	76
CO	Gilpin Co	DENVER AND RIO GRANDE RR-MOFFAT	93	164	0.1%	77
CO	Rio Blanco Co	WILLIAMS FIELD SVCS. - FOUNDATION	95	159	0.1%	79
CO	Moffat Co	QUESTAR PIPELINE CO. EAST HIAWAT.	94	148	0.1%	86
CO	Rio Blanco Co	WILLIAMS FIELD SVCS PICEANCE CRE.	93	117	<0.1%	104
CO	Rio Blanco Co	CHEVRON USA PRODUCTION CO. RANGE	93	113	<0.1%	109
CO	Larimer Co	COLORADO STATE UNIVERSITY	94	111	<0.1%	110
CO	Rio Blanco Co	WILLIAMS FIELD SVCS N DOUGLAS SI.	93	102	<0.1%	115
UT	Duchesne Co	ANR PRODUCTION COMPANY	90	2029	2.3%	7
UT	Uintah Co	CHEVRON USA	90	816	0.9%	14
UT	Daggett Co	QUESTAR PIPELINE CO.	90	741	0.9%	15
UT	Uintah Co	EXXON USA	90	740	0.9%	16
UT	Duchesne Co	GARY REFINERY	90	654	0.8%	17
UT	Uintah Co	CHEVRON USA - WONSITS VALLEY FIELD	90	561	0.6%	20
UT	Duchesne Co	KOCH HYDROCARBONS - CEDAR RIM PL.	90	366	0.4%	25
UT	Duchesne Co	KOCH HYDROCARBON	90	205	0.2%	31
UT	Uintah Co	NATURAL GAS CORP OF CALIFORNIA	90	194	0.2%	32
UT	Duchesne Co	MAXUS EXPLORATION	90	190	0.2%	33
UT	Duchesne Co	CHEVRON PIPELINE	90	171	0.2%	36
UT	Duchesne Co	PENNZOIL	90	165	0.2%	37
UT	Duchesne Co	COASTAL CHEMICAL - MAIN GAS PLNT	90	147	0.2%	40
UT	Duchesne Co	GARY REFINERY	90	140	0.2%	41
UT	Duchesne Co	LOMAX EXPLORATION	90	130	0.2%	42
UT	Uintah Co	WESTROC, INC.	90	123	0.1%	43
UT	Duchesne Co	FLYING J	90	108	0.1%	45

Table 2b (cont.). Emissions Inventory for NO_2 for selected counties[1] in Colorado, Utah, and Wyoming.

State	County	Facility	Yr	Tons/yr	% tot.[2]	Rank[3]
WY	Sweetwater Co	PACIFICORP - JIM BRIDGER	94	30975	23.6%	1
WY	Lincoln Co	PACIFICORP NAUGHTON POWER PLANT	94	18101	13.8%	3
WY	Sweetwater Co	GENERAL CHEMICAL	94	3757	2.9%	6
WY	Sweetwater Co	FMC TRONA	94	2850	2.2%	7
WY	Albany Co	MOUNTAIN CEMENT CO	94	2586	2.0%	8
WY	Sweetwater Co	TEXAS GULF TRONA	94	2285	1.7%	9
WY	Sweetwater Co	SOLVAY MINERALS, INC.	94	2166	1.7%	10
WY	Sweetwater Co	UNION PAC BRADY	94	1384	1.1%	11
WY	Carbon Co	SINCLAIR OIL CORP	94	1292	1.0%	13
WY	Uinta Co	AMOCO ANSCHUTZ RANCH	94	1204	0.9%	15
WY	Carbon Co	CIG RAWLINS COMP	94	1144	0.9%	16
WY	Albany Co	COLORADO INTERSTATE GAS-LARAMIE	94	605	0.5%	26
WY	Sweetwater Co	RHONE-POULENC CHEM	94	544	0.4%	28
WY	Sweetwater Co	UNION PAC PATRICK DR	94	523	0.4%	29
WY	Uinta Co	DRESSER-RAND COMP	94	279	0.2%	36
WY	Sweetwater Co	SF PHOSPHATES, INC	94	239	0.2%	38
WY	Uinta Co	UNIVERSAL RESOURCES CORP - CLEAR	92	166	0.1%	47
WY	Uinta Co	ORYX ENERGY - LUCKY DITCH GAS PL.	94	172	0.1%	49
WY	Uinta Co	AMOCO WHITNEY CANYON	94	159	0.1%	51
WY	Uinta Co	QUESTAR PIPELINE (EAKIN STATION)	93	159	0.1%	53
WY	Uinta Co	UNION PAC EMIGRANT	94	138	0.1%	63
WY	Sweetwater Co	COLORADO INTERSTATE GAS-DESERT S.	94	136	0.1%	67
WY	Uinta Co	CHEVRON USA - PAINTER RESERVOIR	94	131	<0.1%	69
Colorado total emissions: 128362 tons						
Utah total emissions: 86497 tons						
Wyoming total emissions: 131181 tons						

[1]Facilities with NO_2 Emissions ≥ 100 TPY (USEPA, 1994, 1995). Counties in the vicinity of the study area and neighboring states.
[2]Percentage of total emissions for the state.
[3]Rank within the state.

A stratified systematic sampling design with artificial strata was used for the collection of lichens in MZW. Primary sample sites were located at 3-6 km increments[6] along a north-south trending traverse paralleling the Continental Divide within MZW (Figure 3). In general, sample sites were near treeline and usually on the west side of the Continental Divide. At three randomly chosen locations (one per sampling team) within MZW, a site replicate was collected as the second level or strata of the sampling design. A site replicate, (i.e., the secondary site) was defined as a new sample locus about 0.5 km from the primary site position. The third strata in the design was the laboratory analysis of blind sample splits. Although this level is referred to as laboratory error (Tables 8-11), this level includes the variance associated with heterogeneity of the sample, the sample preparation, and the laboratory analysis. Two to three samples, depending upon species and type of analyses, were randomly chosen as laboratory replicates from the pool of all primary and secondary site samples.

The stratified design permits an unbalanced, one-way hierarchical analysis of variance (ANOVA) of spatial variability within MZW and the traverse allows an examination of north-south trends within the MZW. In order to assess the variance attributable to each level in the ANOVA design the following statistical model was used:

$$s_x^2 = s_\alpha^2 + s_\beta^2 + s_\gamma^2$$

where the total variance (s_x^2) is the sum of variances for the variance components for the three hierarchical levels: among sites (s_α^2), site replication (s_β^2), and within-sample heterogeneity, preparation, and laboratory error (s_γ^2). Tests for statistical significance of the difference (*F* test) between levels were made by ratioing the mean square for a level with the mean square for the next lower level. Example statistical results for the ANOVA are given in Appendix IV.

Lichen samples were collected also from other wilderness and national forest lands within about 160 km of MZW (Figure 4, see also Figures A1-A3 in Appendix II). These lichen samples (not including MZW samples) are the regional samples referred to throughout this report. A stratified systematic sampling design like the MZW design was used for the regional sampling. Samples were collected from Eagles Nest, Flat Tops, Maroon Bells, Rawah, Sarvis Creek, and Savage Run Wildernesses, Rocky Mountain National Park, and additional sites within Routt and Medicine Bow National Forests. In general, for each wilderness or other land management unit within the region, samples were collected at two primary sites and one replicate or secondary site. Also, blind sample splits were analyzed by the laboratory. The ANOVA model was similar to the preceding model for MZW, however, it included one additional level for variance among areas within the region. These regional sites provide comparisons with sites from MZW and an examination of regional trends.

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[6]Sample sites were selected primarily based on having a uniform distribution of sample sites along the north-south trending traverse and that met the other site selection criteria including accessibility. The sites were assumed to be randomly selected within the constraints of the stratified systematic sampling design.

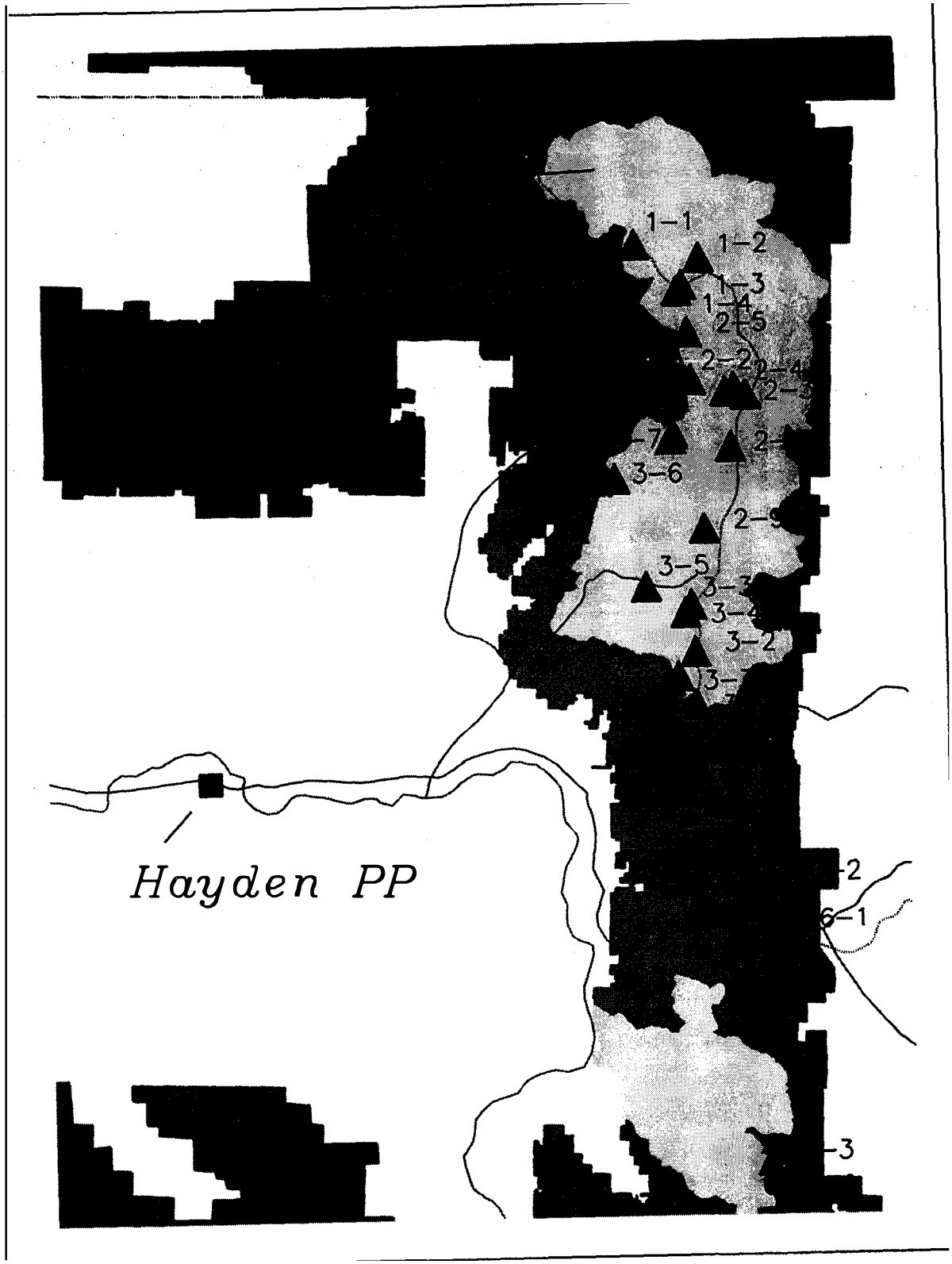

Figure 3. Location of lichen sample sites (▲) in Mt. Zirkel Wilderness and the southern portion of Routt National Forest (map features are approximate).

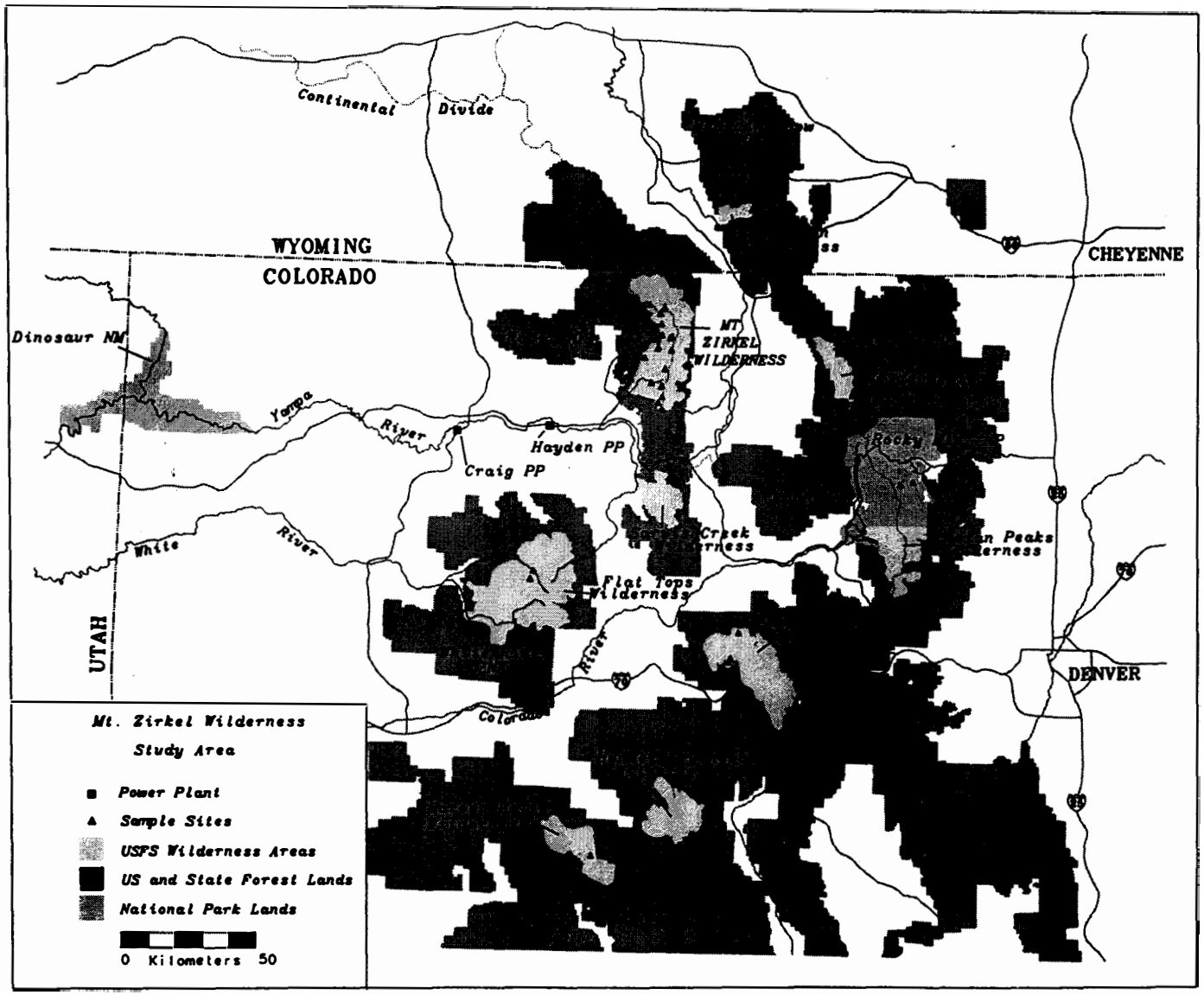

Figure 4. Location of Regional and MZW subalpine sample sites (map features are approximate).

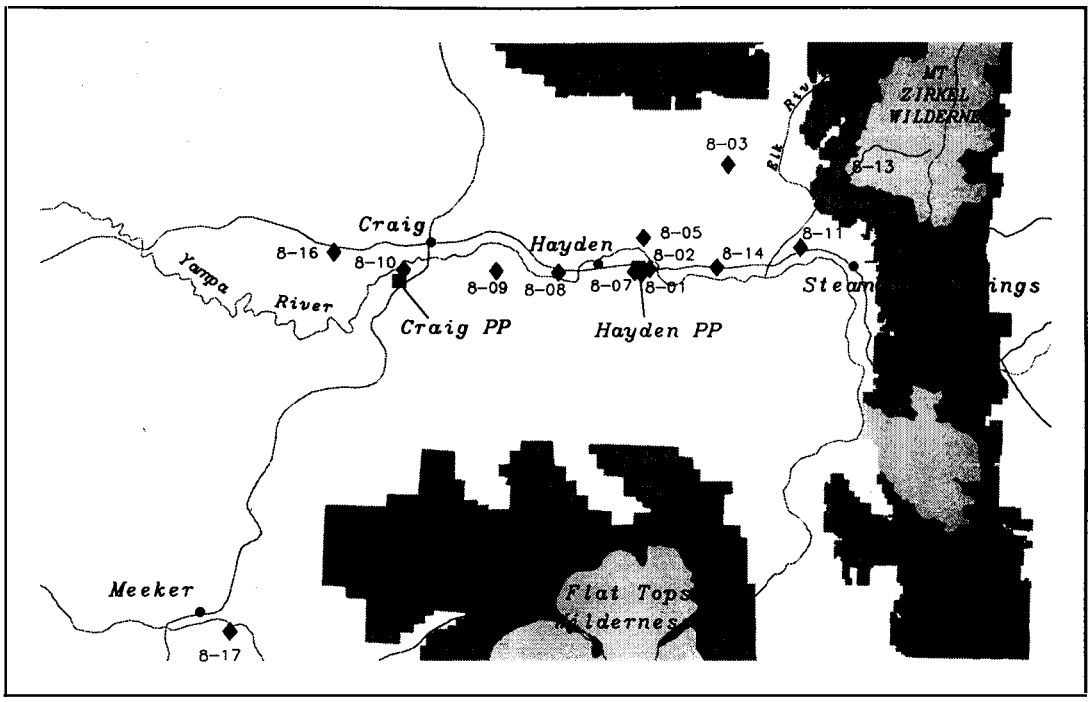

Figure 5a. Location of *Tortula* sample sites (♦) in the Yampa Valley (map features are approximate).

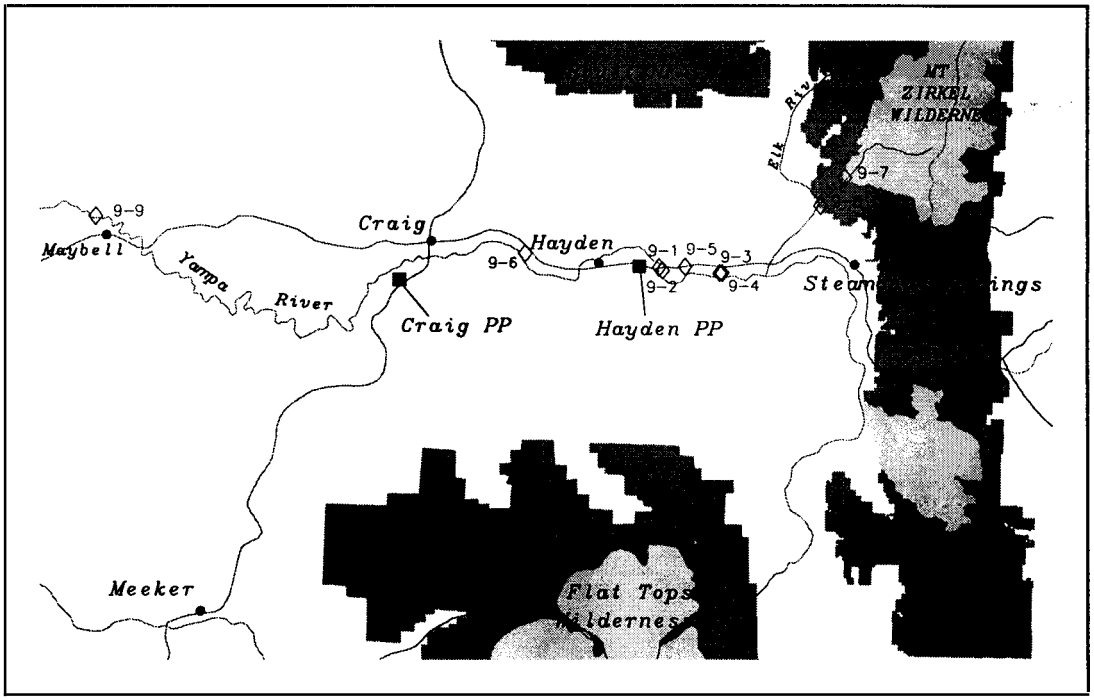

Figure 5b. Location of *Xanthoria* sample sites (◇) in the Yampa Valley (map features are approximate).

Xanthoparmelia cumberlandia was the primary target lichen species at the MZW and regional sample sites. Also, *Usnea lapponica* and *Bryoria fuscescens* were collected, where possible. All site selection criteria and collection methods were alike for the MZW and regional sampling. Sampling sites were pre-selected based on geographic distribution, suspected presence of the target lichens and other site selection criteria described in the next section, proximity of pre-existing snow and lake chemistry study sites, and various logistical considerations such as reasonable accessibility.

Two independent sampling traverses in the riparian and sagebrush zones were made within the east-west corridor of the Yampa River Valley. Lichen (*Xanthoria* spp.) was collected from the riparian zone and moss (*Tortula ruralis*) was collected from the sagebrush zone along the traverses from west of Craig eastward toward MZW (Figure 5a,b). The majority of sites were at geometrically increasing distances eastward of the Hayden Power Station. These traverses were intended for examination of the localized distribution of elements for sites that would have a high probability of being within the zone of influence of the power stations and for an assessment of spatial trends east and west of the power stations.

Numerous constraints, such as accessibility, ability to collect large quantities of an individual lichen species at a site, and budget, limited the number of site and laboratory replicates in the ANOVA's. Replication rates were generally on the order of 10-25% overall. Interpretations related to the variance associated with each of the levels in ANOVA should be viewed with some caution because of the unbalancing of the design. The number of samples for each ANOVA level for the five species used in the MZW, Regional, and Yampa Valley sampling designs are summarized below in the Element Concentration Variance section (Table 7).

Target Lichen and Moss Species

In the subalpine terrain in MZW and at the regional sites, the primary target species was the saxicolous lichen[7], *Xanthoparmelia cumberlandia* (Gyelink) Hale[8]. This lichen was chosen because it is common throughout the region on rock outcrops at elevations from about 2,100 m to more than 3,300 m, i.e., above tree-line. The upper surface of the thallus (leafy tissue) is lobed and greenish yellow with numerous fruiting bodies; the lower surface is tan

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[7]Common lichenological terms used in this report include two terms that refer to the type of substrate on which the lichens grow (i.e., saxicolous--growing on rocks and epiphytic--growing on trees or other plants) and two terms that refer to the growth form of the lichens (i.e., foliose--leaf-like tissue and fruticose--shrubby or hair-like tissue (Hale, 1979)). In this study we collected two lichens with foliose growth form, the saxicolous lichen *Xanthoparmelia* and the epiphytic lichen *Xanthoria*, and two lichens with fruticose growth form, the epiphytic lichens *Bryoria* and *Usnea*.

[8]Taxonomic identifications of lichens and mosses were based on morphological characteristics and chemical spot tests. Lichen species identifications were verified on the habitat voucher specimens by Linda Geiser and Jim Riley (USFS botanist, retired). Moss species identification was verified by John Christy, Ph.D. (a bryologist with the Oregon Natural Heritage Program). Appendix III lists all voucher specimen species identifications.

to brown and moderately rhizinate. Growth is concentric and thalli are 3-20 cm in diameter. The lichen attaches to its rock substrate via rhizines, and can be removed with a knife, albeit with some difficulty (Figure 6) (Hale, 1979). Yet, it was more easily removed from its substrate than any of the other ubiquitous high elevation saxicolous lichens because of its limited surface attachment and foliose growth form. Limited comparative chemical analysis data are available for *X. cumberlandia* from the Flat Tops Wilderness (Hale, 1982; Lichens Unlimited, 1993) and the Buffalo Pass area of Routt National Forest (see Appendix V). The main disadvantage of *Xanthoparmelia* is that it grows over rocks, trapping soil and mineral debris between overlapping thallus lobes and rhizines and under the thallus itself.

Epiphytic (~~i.e., arboreal~~) lichens were a preferable target species to the saxicolous (i.e., rock-growing) lichens, because of a lower potential for substrate contamination. However, reconnaissance work indicated that epiphytic lichens could be beyond reach in the canopy, were generally restricted to narrower, aspect determined elevational bands, and their range never extended into alpine habitats, as did *Xanthoparmelia*. Despite these problems, the epiphytic lichens *Usnea lapponica* Vainio and *Bryoria fuscescens* (Gyelink) Brodo and D. Hawks were collected as secondary target lichen species wherever possible. The *U. lapponica* has a short tufted thallus, mostly <8 cm long, and is pale green with a yellowish tinge. The cylindrical main branches are densely papillate and have few to numerous short side branches bearing strongly concave soralia, which often wrap around and expose the central axis (Figure 7). *B. fuscescens* has a longer, pendant dark brown thallus, typically 5-15 cm long, with finer branches (0.3-0.6 mm diameter) and abundant fissural to tuberculate soralia which are generally broader than the branches on which they occur (Figure 8). Both epiphytic lichen species were found on spruce and fir hosts. Limited chemical analysis data are available for *Usnea* from an ultramafic region in Redwood National Park (Gough and others, 1988).

The lichen species found in the subalpine zone did not extend in range into the Yampa Valley. The most common epiphytic lichens observed in the Yampa Valley were *Xanthoria* species. These were prevalent on cottonwood trunks in the riparian zone along the Yampa River. The predominant species collected was *Xanthoria polycarpa* (Ehrh.) Oliv., intermixed in varying amounts with *Xanthoria fallax* (Hepp.) Arn. *Xanthoria* species have a bright orange thallus, typically less than 1 cm up to 2 cm across, but coalescing in colonies covering larger areas (Figure 9). Individual thalli have minute lobes <1.5 mm broad, tightly appressed at the base to its bark substrate. *X. polycarpa* bears abundant fruiting bodies, whereas *X. fallax* forms soredia on the underside of the lobe tips and fruits only infrequently.

Because macrolichens were not easily found in reasonable quantities in the Yampa Valley sagebrush zone, a terrestrial moss, *Tortula ruralis* (Hedw.) Gaertn., Meyer et Scherb., commonly known as star moss, was collected (Figure 10). This moss grows 1-8 cm tall in dense to loose tufts and was found growing in soil in protected areas such as at the base of sagebrush or in rock crevices. The upper portion of the stem was typically a dark green to lighter green depending upon moisture status. The lower portion was red brown. Individual leaves are strongly squarrose-recurved when wet and the costa (midrib) extends prominently beyond the leaf tip. This species is probably the most common moss in Colorado and Utah and is found in arid to moist areas from lowlands to high elevations (Weber, 1973; Flowers, 1973). Like the rock-growing lichen *Xanthoparmelia*, *T. ruralis* had the

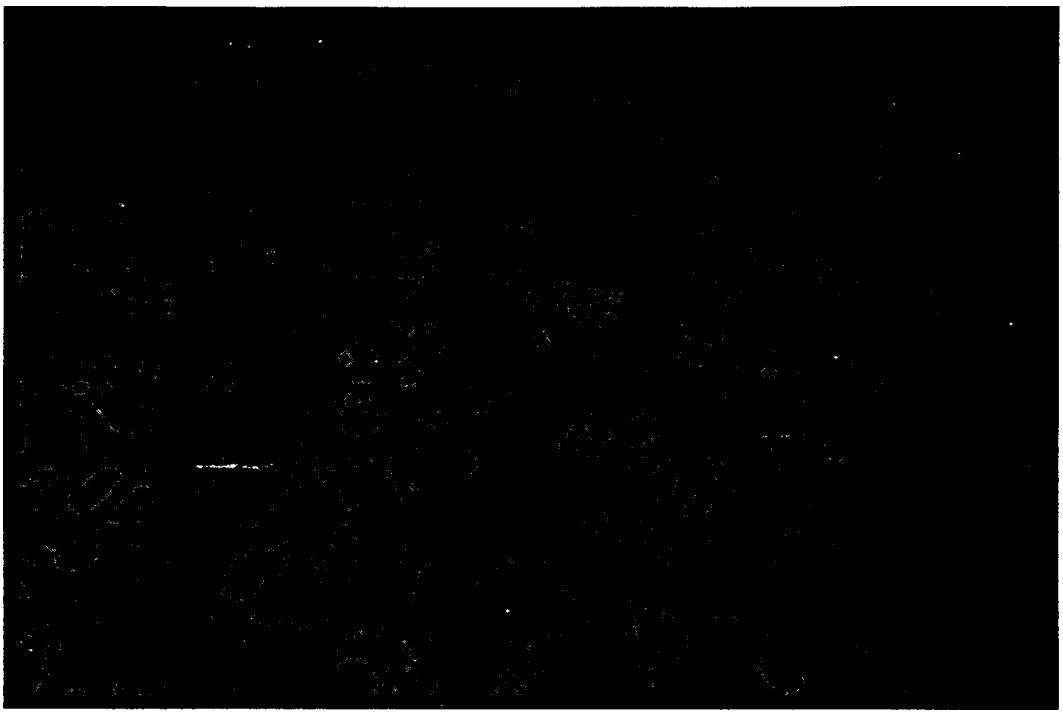

Figure 6. Saxicolous foliose lichen *Xanthoparmelia cumberlandia* in the subalpine zone (photograph courtesy of Stephen Sharnoff and Sylvia Duran Sharnoff © 1996).

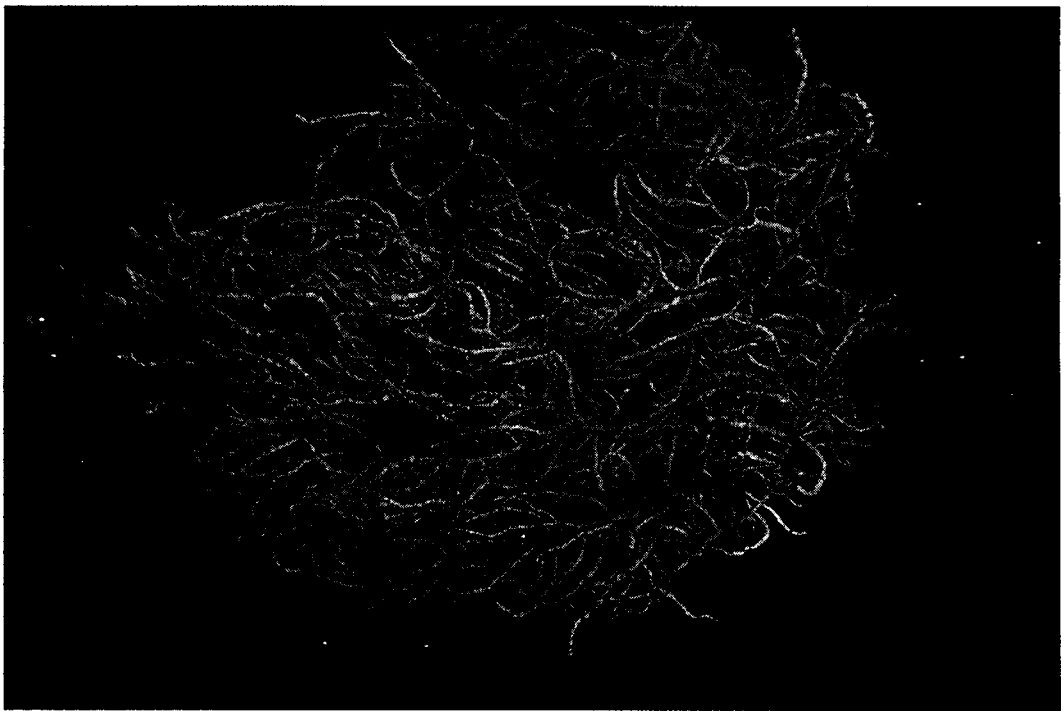

Figure 7. Epiphytic fruticose lichen *Usnea lapponica* in the subalpine zone (photograph courtesy of Stephen Sharnoff and Sylvia Duran Sharnoff © 1996).

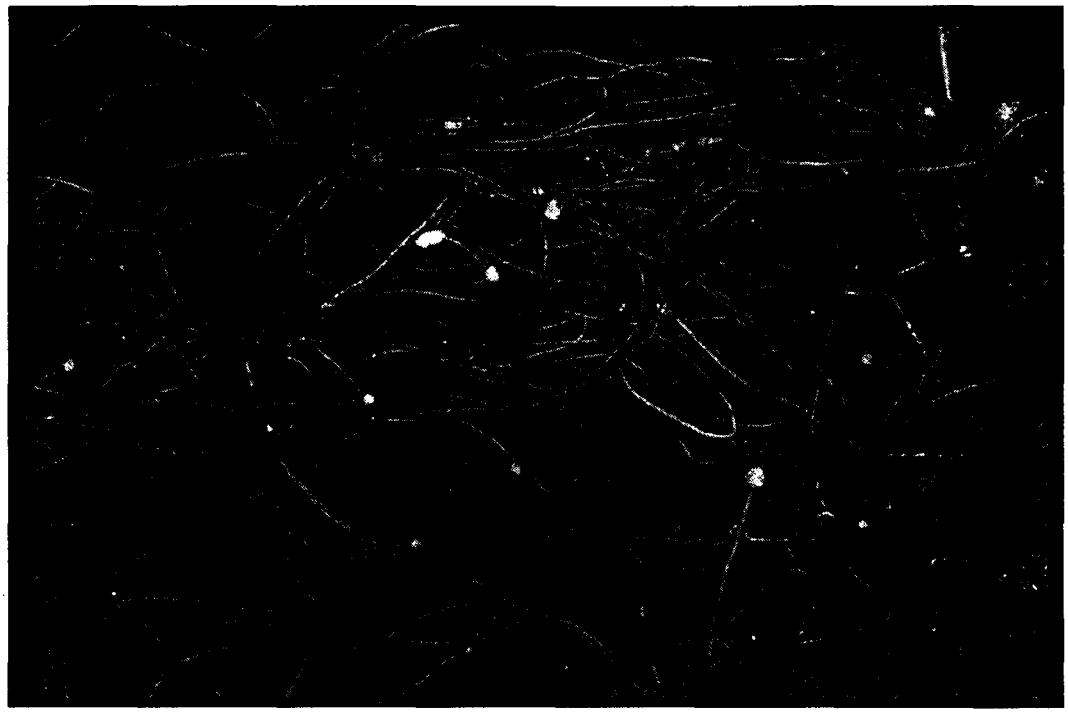

Figure 8. Epiphytic fruticose lichen *Bryoria fuscescens* in the subalpine zone (photograph courtesy of Stephen Sharnoff and Sylvia Duran Sharnoff © 1996).

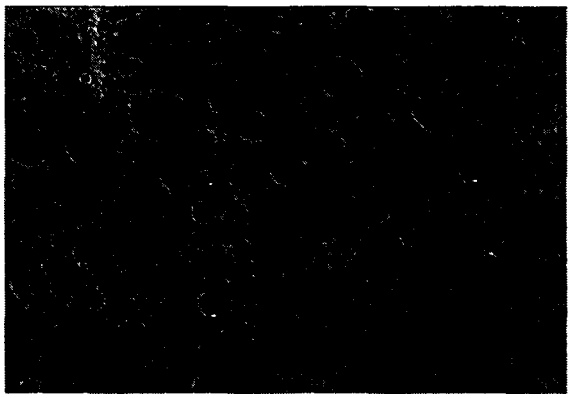

Figure 9a. Epiphytic foliose lichen *Xanthoria polycarpa* in the riparian zone (photograph courtesy of Stephen Sharnoff and Sylvia Duran Sharnoff © 1996).

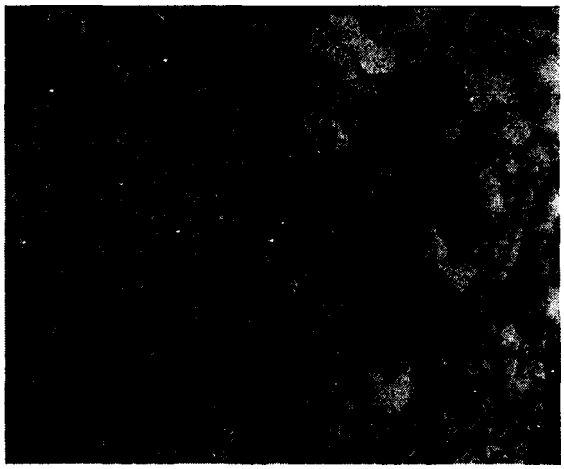

Figure 9b. Epiphytic foliose lichen *Xanthoria fallax* in the riparian zone (photograph courtesy of Stephen Sharnoff and Sylvia Duran Sharnoff © 1996).

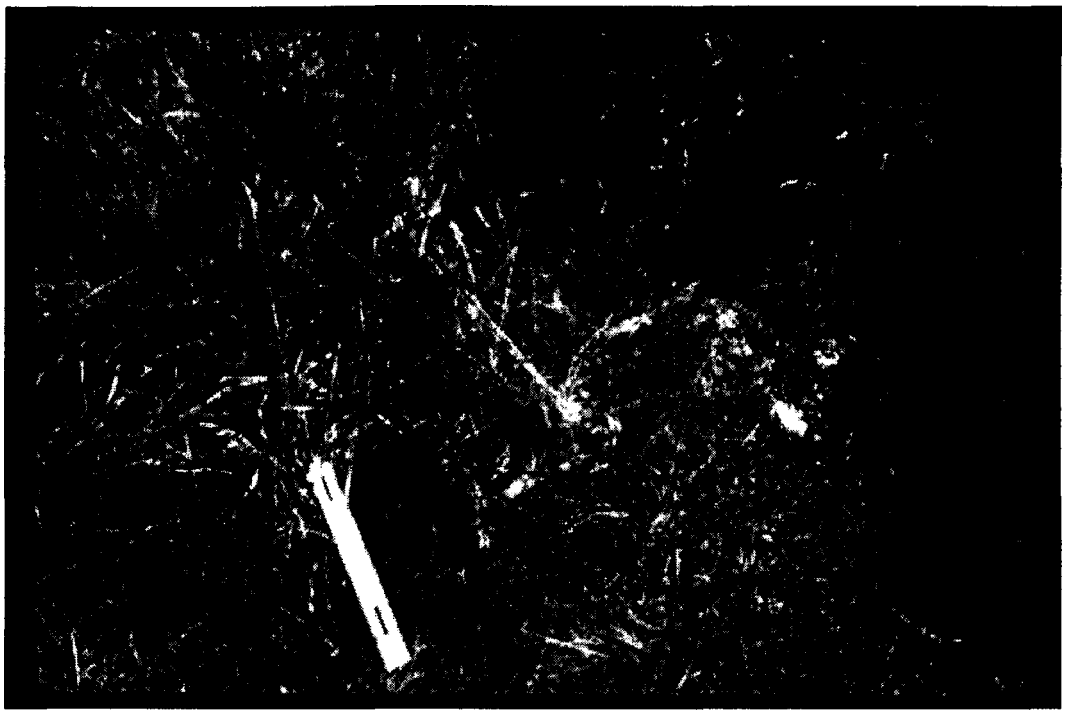

Figure 10a. Moss *Tortula ruralis* at the base of sagebrush in the Yampa Valley.

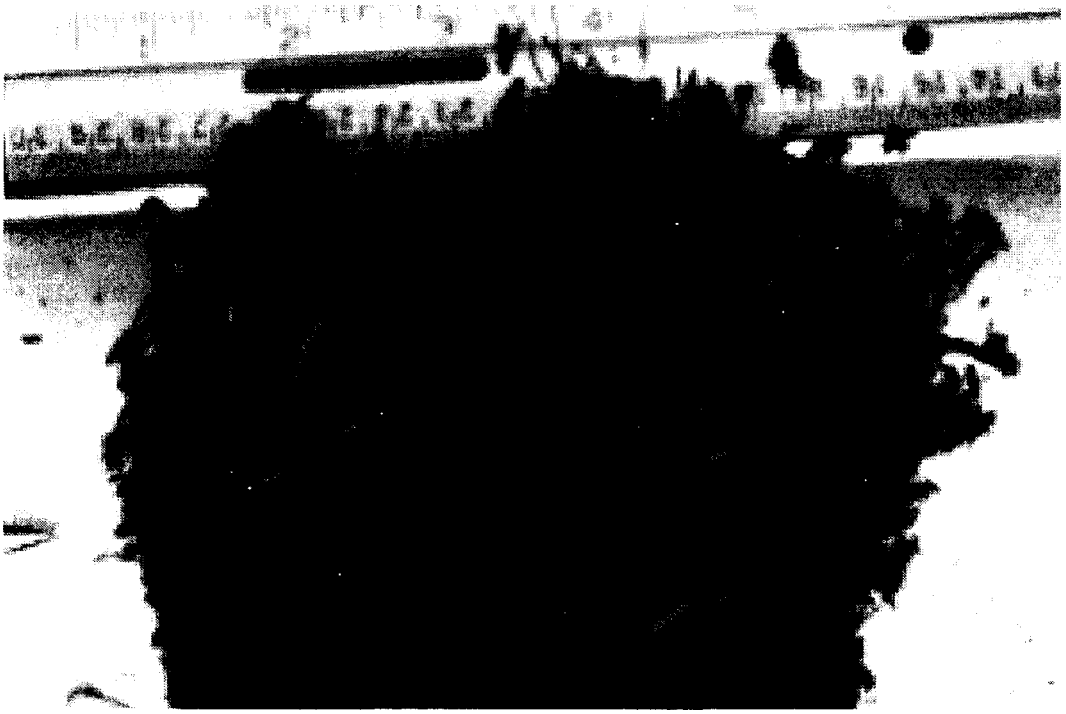

Figure 10b. Moss *Tortula ruralis* from the sagebrush zone.

disadvantage of potential substrate contamination and highly variable ratios of green to red senescent portions of the moss stem. Differences in chemical content of the two portions of the moss have been observed (Bargagli and others, 1995), but what influence this might have on our study is unknown. Differences in the nature of soil among sites and its influence on moss chemistry may play a larger, but equally unquantified role.

STUDY METHODS

Sample Collection

Sample collection for the MZW sites was performed primarily from July 27 through July 29, 1994 by three sampling teams. A few additional sites were collected between July 30 and August 6. Sampling at all regional and Yampa River Valley sites was conducted from August 2-6 by five sampling teams. Sampling teams were composed of two or more members. Team members underwent a study/sampling orientation and all team leaders had field training. Each team followed an established field sampling protocol and recorded sample collection and site description information on preprinted field data sheets (Appendix I).

Although general sample site locations were preselected, each team leader was given the final responsibility for site selection based on the study criteria, local conditions, and safety considerations as outlined in the field sampling protocols. Site selection criteria included factors such as presence of the target lichen species in sufficient quantity, health and status of the specimens, and distance from local sources of contamination such as roads. For the sites in MZW and at the regional sites the saxicolous lichen *Xanthoparmelia cumberlandia* was the primary target lichen species. It was collected as a composite sample[9] from the same rock substrate at 4-10 locations spread over at least 25 m within the sample plot. Each sample plot had a maximum radius of 250 m. Plots were generally west or southwest facing at elevations from 2,700-3,300 m (9,000-11,000 ft) and on the west side of the Continental Divide.

Where possible in MZW and the region, *Usnea lapponica* and *Bryoria fuscescens* were collected also. Because of their distribution, all three lichens were collected infrequently at the same site. Plots for the epiphytic (arboreal) lichens were generally at lower elevations and in more closed canopies. The epiphytic lichens were collected as composite samples from up to 20 trees of whatever tree substrate was available at a site (usually spruce or fir).

Along the Yampa Valley-riparian traverse, *Xanthoria* species were collected from cottonwood tree trunks and lower branches, generally at a height of 1-2 m. A composite sample was collected from 4-10 trees within a radius of 50 m and usually at least 10 m from the edge of the Yampa River. For the Yampa Valley-sagebrush traverse, the moss *Tortula*

[9]All samples were collected as composite samples to provide enough material for analysis, more accurately represent the chemical characteristics of the sample population at the site, and to effectively integrate the receptor characteristics such as lichen size, age, and microhabitat of the individual lichens over a site.

ruralis was collected as a composite sample from around the bases of big sagebrush (*Artemisia tridentata*).

Powder-free gloves were worn by all team members involved in the collection of lichen and moss samples[10]. Lichens and moss were removed from their substrate by hand (*Bryoria*, *Usnea*, or *Tortula*) or by using a stainless steel knife (*Xanthoparmelia* and *Xanthoria*). At each site three types of lichen or moss samples were collected. Several grams of lichen or moss were collected and stored in paper bags as a representative habitat voucher specimen and for verification of field identifications. Fifteen or more grams of lichen or moss were collected and stored in Kapak Corp.[11] polyester bags for chemical analysis. About two grams of material were collected and stored in paper bags for physiological analysis. The physiological samples were stored in the dark in ice chests as soon as possible after collection. In addition, at all locations a 1 kg composite sample of mineral soil was collected. Superficial organic litter and decomposing organic matter were not sampled. At sites where *Xanthoparmelia* was collected, a representative hand sample of the rock substrate was collected, as well. Soil and rock specimens were not chemically analyzed.

Field documentation was composed of five parts: field data sheets, site location maps, site photographs, field team master sample inventory, and a team travel log (Appendix I). Field data sheets were composed of a set of four pages of preprinted forms for each site for recording site specific information. The final part of each set of field data sheets was a field audit. The audit section was completed by a member of the field team that did not record the site description information. The audit consisted of a review of the field data sheets for completeness and legibility, verification of all sample labeling for correctness and legibility, and completion of the master sample inventory. The master sample inventory was used for the transfer of samples from the field team to the project principals at the field headquarters.

Each sample site was identified by a unique site identifier composed of plot number, the collection date, and team member initials. A simplified site number is used throughout the text which is composed of the team number and the original plot number. A list of all sample sites and their site identifiers is in Appendix II. Site location coordinates and elevations were generally determined from 1:24000 scale U.S. Geological Survey quadrangle maps as recorded by the field teams. Global positioning satellite (GPS) receivers were used by some field teams to record site locations. Where available, the GPS locations were used for confirmation of the location recorded on the field maps and shown in Appendix II.

Sample Site Characteristics

Bryoria was collected at a total of 16 sites (including the 3 replicate sites) in the subalpine zone. The elevation of the sites averaged 2,830 m in MZW and 2,950 m in the region. Although *Usnea* and *Bryoria* were usually collected at the same site, *Usnea* was

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[10]As a result of the precautions taken during sampling, sample preparation, and chemical analysis potential contamination of the samples is expected to be minimal at most and not influence the interpretative results of this study. This is particularly true for several of the major elements such as S and N.

[11]Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

collected at a few more sites (22). The elevation of the sites were similar to the *Bryoria* sites (averaged 2,860 m in MZW and 2,970 m in the region). For both species, the regional sites were slightly higher than the MZW sites by about 100 m. Within MZW, *Xanthoparmelia* was collected at higher elevations (16 sites at an average elevation of 3,120 m) than the other two lichens by about 300 m, whereas at the regional sites the average elevation for *Xanthoparmelia* (19 sites at an average elevation of 2,990 m) was about the same as the other lichens. Although there were relatively small differences in elevation between the MZW and regional sites, there was a more significant difference in precipitation between the sites[12] (Figure 11). For example, using the 35 *Xanthoparmelia* sites, the average annual precipitation within MZW area was 130 cm, whereas it averaged 88 cm at the regional sites. The MZW sites also averaged about 50 km from the Hayden Power Station[13]. Sites in Flat Tops Wilderness and southern Routt National Forest were also close to the Hayden station (< 60 km), whereas all other regional sites ranged from 100 to 160 km away.

Because there is a high inverse correlation between the independent variables of average precipitation and distance from the Hayden station, it is difficult to untangle what may be the biogeochemical influences on the lichens of these two variables. Also, because elevation and precipitation generally correlate, a similar situation arises. However, we speculate that high precipitation amounts and close proximity to the power stations are synergistic parameters that provide for the greatest amount of potential pollutant deposition.

Within the Yampa Valley, *Tortula* was collected at 14 sites and *Xanthoria* at 9 sites (*Xanthoria* was collected at two additional sites, but the data are not usually included in the analyses because of differences in substrate and ecozone). Elevation and precipitation generally increase from west to east in the valley. Elevations for *Tortula* and *Xanthoria* ranged from 1,800 to 2,320 m and precipitation ranged from less than 25 cm to about 75 cm. For the sites east of the Hayden Power Station, it is difficult to assess which of the covarying parameters may have more influence on the lichen and moss collected: elevation, precipitation, or distance from the power stations, or even lithology.

Sample Preparation

Lichen and moss samples were air dried in nylon mesh bags in the field or at the field headquarters when necessary as described in the sampling protocol. At the field headquarters or at the laboratory, each sample was cleaned by hand to remove extraneous material such as organic detritus, other lichen or moss species, or adhering substrate particles such as bark or

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[12]The isohyetal map of average annual precipitation for 1951-1980 (Doesken and others, 1984) was based on limited high elevation precipitation data with modeling of precipitation patterns over complex terrain. Although the accuracy of precipitation estimated for a specific location may not be high, general trends for regions are believed to be reasonably accurate. The annual variability in precipitation for a specific location may also be high, but long term averages appear to have changed little for northwest Colorado when comparing the 30-year average for 1951-1980 with 1961-1990 (i.e., 0-1 inch wetter in 1961-1990 (Doesken, 1991)).

[13]Distances are arbitrarily referenced to the Hayden Power Station. Distances from the Craig Power Station are provided in Appendix II.

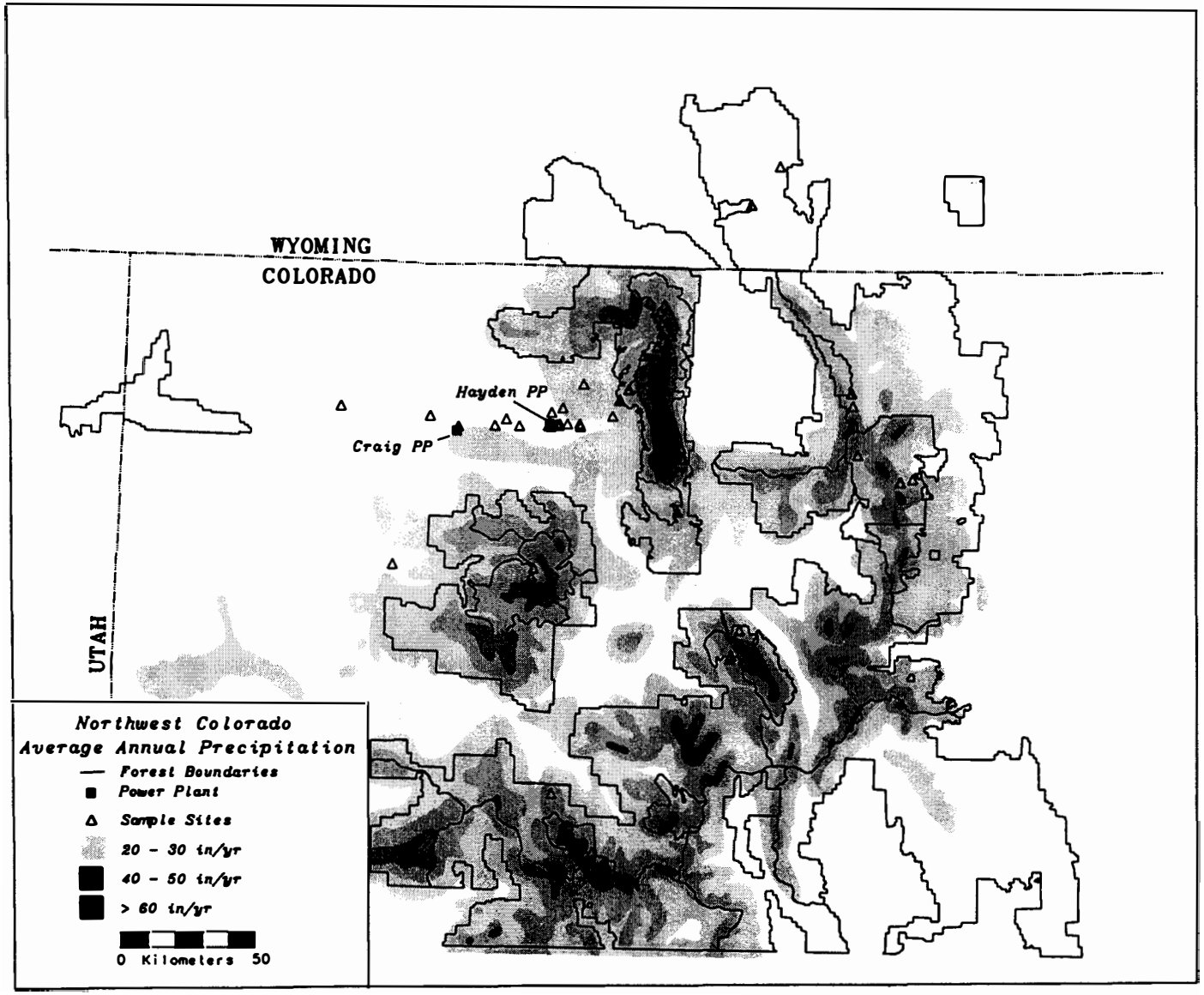

Figure 11. Average annual precipitation for northwest Colorado (after Doesken et al., 1984). Zones of annual precipitation increments: 20-30, 30-40, 40-50, 50-60, and >60 in/yr are illustrated with increasing gray-scale tone, respectively.

rock. Then the hand-cleaned material was washed to remove surface contaminants such as soil or dust[14]. The washing procedure consisted of hydrating the lichen sample with a fine mist of deionized water followed by five deionized water washes in an ultrasonic bath. The entire sample was placed in a beaker filled with about 1 L of deionized water. The beaker and sample were placed in an ultrasonic bath for 30 sec. The sample was placed in a clean beaker with clean deionized water and sonicated another time for 30 sec. After five ultrasonication/clean water washes, the sample was dried in an oven at 35°C for about 48 hrs. Personnel wore powder-free gloves during all sample handling steps.

The oven-dried lichen sample was placed in a large ceramic mortar and it was frozen with liquid nitrogen. Then the frozen sample was ground by hand with a ceramic pestle to a relatively uniform fine particle size. The oven-dried moss samples were ground mechanically with stainless steel blades in a Wiley mill to pass a 1 mm sieve. The ground material of lichens and moss was split as necessary for submission to the various laboratories and for the blind laboratory splits. All samples and blind splits within a suite of lichen or moss species were randomized and assigned sequential laboratory numbers. National Institute of Standards and Technology (NIST) standard reference materials (SRM) were also submitted to the laboratories blind and randomized within the sample suites.

Representative coal samples for the Trapper and Seneca 2 coal mines were obtained from the USGS Coal Quality Sample Archives. Ground subsamples from one benched channel sample in the Trapper Mine were available to make one depth-weighted composite sample representing the approximately 3 m thick Q coal seam. Subsamples from four drill cores in the Seneca 2 Mine were composited within each core to represent the 2-3 m thick Wadge coal seam. Each composite sample was thoroughly mixed and submitted for sulfur isotope determinations. Two of the five composite coal samples, one from each mine, were submitted for lead isotope analyses.

Chemical Analysis

Major and trace elements in all samples of lichens and mosses were determined by the University of Minnesota Soil Testing and Research Analytical Laboratories (UMSTRAL). As described above, the ground samples ($\sim$5 g each) were submitted to the laboratory in randomized suites that included blind sample splits and standard reference materials. The laboratory dried the samples in an oven at 65°C for 48 hrs prior to any analyses. Total sulfur was determined by combusting 200 mg of sample mixed with 500 mg of V_2O_5 in an oxygen atmosphere at 1370°C in a Leco Corp. SC-132 Sulfur Analzyer. The SO_2 evolved from the

[14]Washing of the lichen and moss samples was conducted to remove dust, rock, soil, vegetation, and other detrital material loosely adhering to the surface of the samples. Washing does not remove all of the surficial material (Gough and Erdman, 1977). Although pollutant contamination of vegetation is often considered to include what is on the surface in addition to what is in the vegetation, for samples subject to eolian dust or soil contamination of vegetation such as the foliose lichen *Xanthoparmelia* and the moss *Tortula*, excessive dust on the surface may make it difficult to discriminate between what is in the vegetation versus on it and whether the source is predominantly natural or anthropogenic origin. Therefore, washing of these specimens was done to minimize the influence of eolian dust or soil on the chemical results. This procedure also reduces our potential for detecting anthropogenic surface contamination such as fly ash.

Table 3. UMSTRAL determination limits for element concentrations in lichens and moss (determination limits are based on dry-weight of sample).

Element	Determination limit	Element	Determination limit
Al, µg/g	3.6	Mn, µg/g	0.06
As, µg/g	0.78	Mo, µg/g	0.22
Ash, %	0.5	N, %	0.01
B, µg/g	0.46	Na, µg/g	3.6
Ba, µg/g	0.12	Ni, µg/g	0.44
Be, µg/g	0.04	P, µg/g	0.7
Ca, µg/g	0.82	Pb, µg/g	1.7
Cd, µg/g	0.12	Rb, µg/g	53
Co, µg/g	0.24	S, %	0.01
Cr, µg/g	0.28	Si, µg/g	1
Cu, µg/g	0.52	Sr, µg/g	0.06
Fe, µg/g	0.34	Ti, µg/g	0.3
K, µg/g	14	V, µg/g	0.36
Li, µg/g	0.4	Zn, µg/g	0.14
Mg, µg/g	3.8		

sample was determined by a nondispersive infrared detector empirically calibrated with Leco coal reference materials (UMSTRAL, 1992). Total Kjeldahl nitrogen was determined by digesting 150 mg of the dried sample in sulfuric acid with a selenium reducing agent. The ammonium produced was determined colorimetrically with a continuous flow autoanalyzer (UMSTRAL, 1993a). A nitrate reduction step was not included in the digestion procedure. The percentage ash yield was determined by combusting 1 g of the oven-dried sample at 485°C for 12 hrs in a circulating air muffle furnace (UMSTRAL, 1993b).

Other major and trace elements were determined by using a simultaneous multielement inductively coupled-atomic emission spectrometer (ICP-AES). The elements determined and their determination limits are listed in Table 3. In this determination, 0.5 g of dried sample were ashed in the same fashion as the ash yield was determined. The ash was digested in 5 ml of 20% HCl for 30 min at 180-200°C. After heating, the digestion solution was brought to a total volume of 10 ml with deionized water. Residual ash was allowed to settle for a minimum of 3 hrs and the supernatant was analyzed by ICP-AES (UMSTRAL, 1993c). The procedure is only a partial digestion of the sample that is designed to solubilize the less refractory components of plant material. Silicate matrices that may be

present as contaminants of the sample are not as completely solubilized in this procedure as the plant tissue.

Stable sulfur isotope ratios of selected samples of *Xanthoparmelia*, *Usnea*, and *Tortula*, blind sample splits, five composite coal samples, and two botanical SRMs were determined by Coastal Science Laboratories. A total of up to 5 g of sample, 1 g at a time, was combusted in a Parr bomb under a high pressure oxygen atmosphere. After each combustion the bomb was washed and the washings were combined. Barium sulfate was precipitated from the wash solution. The stable sulfur isotope ratio for the sample was determined on the $BaSO_4$ with thermal ionization mass spectrometry. The sulfur isotope ratio is measured in the sample relative to the isotope ratio in a meteoritic troilite standard. The enrichment factor determined is expressed as $\delta^{34}S$ in parts per thousand (‰) or per mil:

$$\delta^{34}S \text{ ‰} = \left[\frac{(^{34}S/^{32}S)_{sample}}{(^{34}S/^{32}S)_{meteorite}} - 1 \right] x \ 1000$$

Lead isotope ratios for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$, were determined in selected samples of *Xanthoparmelia*, *Tortula*, and two whole coal composite samples by the U.S. Geological Survey with a method similar to the procedure outlined by Church (1993). The lichen and moss samples were wet ashed, whereas the coal samples were dry ashed at 500°C prior to acid digestion. The plant material and the coal ash were digested with nitric and perchloric acids in a pressure bomb digestion. After the decomposition steps, the samples were taken to dryness and then dissolved in nitric acid. Iron and ammonium hydroxide were added to the nitric acid solution and the lead was removed from solution as a coprecipitate with iron hydroxide. The lead-iron hydroxide precipitate was dissolved in ultraclean HBr and the lead was further cleaned up in a series of ion exchange steps. Then the lead isotope ratios were determined by loading the sample onto a rhenium filament that was analyzed in a solid-source, thermal-emission mass spectrometer. The data were corrected for thermal fractionation by using a running-average correction technique based on coincident analyses of the NIST natural lead metal SRM 981.

Physiological Analysis

To prevent physiological deterioration that occurs in lichens stored at room temperatures for extensive periods of time, all material was frozen immediately upon arrival at the laboratory.[15] Before experiments were started the material was defrosted slowly and

[15]Although attempts were made to keep lichen samples cool from the time of collection until received at the laboratory, up to one week may have passed between collection and freezing. The influence of being stored in the sampling bag and the transportation time on the status of the physiological functions is unknown. In the future the influence of various field sample handling procedures and a rigorous comparison of field and laboratory measurements needs to be done to test the veracity and robustness of the physiological function test for studies of this sort.

kept under standard conditions of 15°C and 12 hours of light (300 μmol Phot. m^{-2} s^{-1}) followed by 12 hours of dark for 4 days. The specimens were sprayed with distilled water once every morning to simulate a moist/dry cycle.

All visible rock, soil, and other organic matter were removed from the lichen and moss samples by hand. The lichen samples were then divided into three replicates, if adequate material was present. After cleaning the moss, the top 1 cm of the green portion of the plants was cut off and used for physiological analyses. The green portion of the moss was divided into replicates for analyses in a similar fashion to the lichens.

Prior to gas-exchange measurements, samples were sprayed with water and allowed to resaturate in a growth chamber under standard conditions for 30 minutes. Then, the thalli were blotted dry to remove external water droplets and to reach constant water content among samples. The desired water content to obtain optimal and constant levels of photosynthesis varied among species within the range of 80-150% (weight of water/dry weight of lichen). Water content within a species varied less than about 30%. Upon bringing the samples to the appropriate water content, they were placed quickly into the cuvettes of the gas-exchange system.

To measure CO_2 gas-exchange, an open, flow through system was used with precision monitoring of air flow through 4 cuvettes and continuous environmental parameter regulation and measurement of gas exchange. To reduce inherent, transient CO_2 concentrations in the air supply, air was initially mixed in a 200 l carboy and then passed through an activated charcoal trap to remove any background air pollutants. Pressurized house air provided for an even and well regulated air flow of 0.5 l min^{-1} through each teflon-lined aluminum cuvette. To control temperature, the cuvettes were submerged in a water bath kept at 15°C. Prior to entering the cuvettes, the air stream was humidified by passing through a flask filled with deionized water, and then precise humidity regulation of 97% (without subsequent water condensation in the cuvettes) was achieved by using a measuring gas cooler (Walz, MGK1), that cooled the air down to 15°C dew point and removed condensed water. Because lichens have no stomatal control over their water status, controlled high humidities are essential to maintain lichen water status during a measuring cycle and hence allow repeatability of experiments at chosen water content ranges. A timeable gas handling unit (Analytical Development Co. model WA-161) directed the reference air stream, and alternately one of the three measuring air streams to an infrared gas analyzer (LiCor 6262). Net photosynthesis was measured with glass lids on the cuvettes and a 400 W metal halide lamp above the water bath, which resulted in 150 μmol Phot. m^{-2} s^{-1} inside the cuvettes. All millivolt measurements were stored in a data logger (Campbell 21x) for subsequent microcomputer processing.

To characterize the status of photosystem II (PSII), the fast induction curve of chlorophyll fluorescence was determined with a modulation fluorometer (PAM, Walz) using a PAM 102 unit to generate actinic light of 20 watts m^{-2} intensity and a PAM 101 unit for fluorescence measurement. The samples were resaturated as described above and then dark adapted for 15 minutes, after which the fiber optic was placed 1 cm from the lichen surface. The nomenclature used for the fluorescence curves is F_o = fluorescence yield when all PSII reaction centers are open, F_m = maximum fluorescence yield when PSII reaction centers are closed, F_v = variable fluorescence (i.e., $F_v = F_m - F_o$), F_v/F_m = photon yield of PSII photochemistry according to model of Kitajima and Butler (1975). All fluorescence data are

measured in relative fluorescence units. The ratio, F_v/F_m, is used frequently as a measure of stress.

Chlorophylls and related pigments were extracted from the lichens and moss with dimethyl sulfoxide (DMSO) following Ronen & Galun (1984). Duplicate samples of 0.02 g of air-dried lichen were extracted in 10 ml of DMSO and the absorption of the extracts was determined at 415, 435, 646.8, 663.2 and 700 nm wavelengths in a spectrophotometer (Bausch & Lomb Spectronic 1001). The ratio OD435/OD415 was used to determine the breakdown of chlorophyll to phaeophytin. Chlorophyll-a concentrations were calculated from optical densities at 646.8 and 663.2 nm. Pretreatments with acetone were performed on all lichen samples to eliminate interference of lichen acids.

Laboratory Quality Control

In the project quality control (QC) program, blind NIST SRMs and sample splits were submitted to the UMSTRAL and Coastal Science Laboratories as part of the randomized sample suites. Included in the suites of lichen and moss samples that were submitted to UMSTRAL were four splits of SRM 1547, Peach Leaves, four splits of SRM 1575, Pine Needles, and two splits of SRM 1633b, Coal Fly Ash. The results for major and trace element determinations by the UMSTRAL laboratory are shown in Table 4 along with the NIST certified and non-certified values and other literature values. The uncertainty associated with the NIST certified values are listed in NIST's Certificates of Analysis (not included here). The NIST and literature values are based on a total analysis of the SRMs and not a partial digestion procedure as used by the UMSTRAL laboratory. Thus, comparison of the UMSTRAL results for the elements determined by ICP-AES with the NIST values is an evaluation of recovery as well as accuracy. Analytical bias towards low values in the quantification step is not distinguishable from incomplete release of elements from the sample ash in the digestion step.

For many elements, the recovery was from 85-110% for the two botanical SRMs. However, results for As, Co, Mo, and V were generally high by a factor of two or more for both SRMs. Although the results for these four elements are near the determination limits of the analysis method where more error is expected, results for As, Co, Mo, and V should be viewed with extreme caution. Results for Cd, Ni, and Pb also were high for one of the SRMs and the results should be viewed with some caution, but they have not been eliminated from the evaluation sections of this report. High values may be the result of inadequate corrections for blank concentrations or interelement spectroscopic interferences, an absolute bias of a small concentration (e.g., 1 μg/g Pb added to all samples), or a relative bias affecting all concentrations proportionately. Insufficient data are available in this study to identify the exact nature of the error for these elements.

For the one botanical SRM where a published value for comparison existed, titanium had less than 25% recovery. No values for Si are available for comparison, but we suspect that Si recovery was at least as poor as for Ti. Recoveries for elements from the coal fly ash SRM were generally less than 40%, with recovery for Al, Ti, and Si being 10%, 8%, and 1%, respectively. These results suggest that the HCl digestion procedure is particularly ineffective at attacking an alumino-silicate matrix. Thus, the digestion procedure should

Table 4a. Summary of analysis results on a dry-weight basis for botanical standard reference materials.

	NIST SRM 1547, Peach Leaves			NIST SRM 1575, Pine Needles			
	This work		NIST	This work		NIST	Literature
Element	Mean[1]	Std. Dev.[2]	value[3]	Mean[1]	Std. Dev.[2]	value[3]	value[4]
N%	2.58	0.14	(2.96)	1.1	0.05	(1.2)	1.20
S%	0.17	0.004	(0.2)	0.12	0.007	-	0.13
Ash %	9.36	0.09	-	2.62	0.04	-	2.69
Al µg/g	228	3	249	454	7	545	510
As µg/g	1.2	0.2	0.06	< 0.8	-	0.21	
B µg/g	26.6	0.5	29	16.8	0.4	-	
Ba µg/g	110	2	124	6.0	0.5	-	7.2
Be µg/g	< 0.04	-	-	< 0.04	-	-	
Ca µg/g	15200	300	15600	4280	70	4100	4200
Cd µg/g	0.1	0.08	(0.03)	0.3	0	(< 0.5)	0.22
Co µg/g	0.6	0.08	(0.07)	0.3	0.08	(0.1)	0.12
Cr µg/g	1.1	0.08	(1)	1.9	0.10	2.6	2.6
Cu µg/g	3.8	0.1	3.7	2.8	0.10	3	3
Fe µg/g	201	3	(220)	173	13	200	185
K µg/g	22800	300	24300	3480	30	3700	3700
Li µg/g	< 0.4	-	-	< 0.4	-	-	0.34
Mg µg/g	4180	60	4320	1140	10	-	1200
Mn µg/g	94	2	98	688	16	675	650
Mo µg/g	0.2	0.1	0.06	0.3	0.05	-	0.15
Na µg/g	26	3	24	19	1	-	50
Ni µg/g	0.9	0.2	0.69	1.8	0.1	(3.5)	2.5
P µg/g	1340	20	(1370)	1150	10	1200	1200
Pb µg/g	2	0.6	0.87	12	0	10.8	10.7
Rb µg/g	< 53	-	(19)	< 53	-	11.7	
Si µg/g	324	11	-	223	11	-	
Sr µg/g	50	0.6	53	4.07	0.05	4.8	5
Ti µg/g	4.6	0.3	-	3.4	0.2	-	14
V µg/g	1.0	0.1	0.37	0.7	0.1	-	0.39
Zn µg/g	17.6	0.2	17.9	85	30	-	67

[1] Arithmetic average of four analyses. [2] NIST values from Certificate of Analysis for each reference material; values in parentheses are non-certified values. [4] Published values from Gladney and others (1987) and Jackson and others (1995).

Table 4b. Summary of analysis results for coal fly ash standard reference material.

	NIST SRM 1633b, Coal Fly Ash			
	This work			
Element	Mean[1]	Std. Dev.[2]	NIST value[3]	% Recovery
N%	0.01	0	-	-
S%	0.18	0.01	0.2075	87
Ash %	97.9	0.2	-	-
Al µg/g	15200	900	150500	10
As µg/g	127	1	136	93
B µg/g	48	3	-	-
Ba µg/g	180	6	709	25
Be µg/g	3.6	0.2	-	-
Ca µg/g	8560	370	15100	57
Cd µg/g	1.0	0.1	0.784	128
Co µg/g	< 0.96	-	(50)	-
Cr µg/g	36	1	198	18
Cu µg/g	43	2	112.8	38
Fe µg/g	21400	1000	77800	28
K µg/g	2000	100	19500	10
Li µg/g	34	1	-	-
Mg µg/g	980	60	4820	20
Mn µg/g	44	2	131.8	33
Mo µg/g	21.6	0.5	-	-
Na µg/g	280	20	2010	14
Ni µg/g	37	2	120.6	31
P µg/g	1290	80	(2300)	56
Pb µg/g	28	2	68.2	41
Rb µg/g	< 210	-	140	-
Si µg/g	1720	10	230200	1
Sr µg/g	380	10	1041	37
Ti µg/g	640	40	7910	8
V µg/g	102	4	295.7	34
Zn µg/g	69	4	(210)	33

[1] Arithmetic average of two analyses. [2] NIST values from Certificate of Analysis; values in parentheses are non-certified values.

Table 5. Lead and sulfur isotope ratios in standard reference materials.

NIST SRM	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
SRM 1571 Orchard Leaves	18.311	15.585	38.118
SRM 1571 Orchard Leaves	18.306	15.579	38.101
SRM 1575 Pine Needles	18.500	15.598	38.160
SRM 1571 Pine Needles	18.500	15.605	38.159
SRM 1633b Coal Fly Ash	18.855	15.647	38.706

	$\delta^{34}S$, ‰	$\delta^{34}S$, ‰
SRM 1547 Peach Leaves	+7.6	+7.8
SRM 1571 Pine Needles	+2.0	+2.3

preferentially discriminate against dissolving potential fly ash or soil contaminants on the surface of lichen or moss tissue. However, the extent to which this digestion will dissolve the wide variety of potential surface contaminants is unknown and even partial dissolution may contribute significant quantities of some elements to the apparent concentration in the lichen tissue.

Sulfur and lead isotope ratios were determined for several NIST SRMs (Table 5). These analyses indicate excellent precision for the techniques. Although these data serve as reference data for future studies, no published values for accuracy comparisons are available for the current study.

As mentioned above, blind sample splits were submitted to UMSTRAL randomized within the sample suites. About 15-25% of the samples were split, depending upon the species. For example, 20% of *Xanthoparmelia* samples were split and analyzed as blind duplicates. In addition, the laboratory analyzed several samples in duplicate. All duplicate results are listed in Appendix III. The blind duplicate analyses were examined as part of the hierarchical analysis of variance. Also, a quality control material, the lichen *Alectoria sarmentosa*, developed for studies of national forest lands in the Pacific Northwest (Geiser, unpublished data) was analyzed numerous times by UMSTRAL as part of our sample suites. The results are listed in Table 6. For those elements that were present in the *A. sarmentosa* at concentrations significantly greater than the determination limit, the precision was generally quite good (i.e., RSD $<$ 5%).

Data Analysis

Data analyses were done by using SYSTAT® (SPSS, Inc., Chicago, IL) statistical software, the USGS Statpac library (Grundy and Miesch, 1988), and various other commercial software on an IBM-compatible personal computer. All vegetation data were

Table 6. Chemical analysis results for *Alectoria sarmentosa* control sample.

UM lab #	N, % (TKN)	S, %	Ash, %	Al, µg/g	As, µg/g	B, µg/g	Ba, µg/g	Be, µg/g	Ca, µg/g
Alectoria-1	0.37	0.04	1.2	83	< 0.8	1.5	3.3	< 0.04	3140
Alectoria-2	0.32	0.04	1.2	80	< 0.8	0.7	3.3	< 0.04	3100
Alectoria-3	0.30	0.04	1.2	79	< 0.8	0.8	3.2	< 0.04	3120
Alectoria-4	0.31	0.03	1.2	76	< 0.8	0.6	3.3	< 0.04	3110
Alectoria-5	0.34	0.03	1.2	80	< 0.8	0.7	3.3	< 0.04	3160
Alectoria-6	0.30	0.03	1.2	78	< 0.8	0.5	3.3	< 0.04	2990
Alectoria-7	0.27	0.03	1.2	77	< 0.8	0.6	3.2	< 0.04	2980
Alectoria-8	0.37	0.04	1.2	80	< 0.8	0.6	3.2	< 0.04	3020
Alectoria-9	0.30	0.03	1.2	--	--	--	--	--	--
Alectoria-10	--	0.04	1.2	--	--	--	--	--	--
Mean	0.32	0.04[3]	1.2	79	< 0.8	0.8	3.3	< 0.04	3080
SD[1]	0.03	0.005	0	2	--	0.3	0.1	--	70
RSD[2], %	11	15	0	3	--	42	2	--	2

UM lab #	Cd, µg/g	Co, µg/g	Cr, µg/g	Cu, µg/g	Fe, µg/g	K, µg/g	Li, µg/g	Mg, µg/g	Mn, µg/g
Alectoria-1	< 0.1	< 0.24	< 0.3	1.0	61.9	1550	< 0.4	294	95.5
Alectoria-2	< 0.1	< 0.24	0.3	1.0	64.8	1530	< 0.4	289	94.6
Alectoria-3	0.2	0.3	0.4	1.2	63.2	1520	< 0.4	292	94.9
Alectoria-4	0.1	< 0.24	0.3	0.9	61.5	1540	< 0.4	293	96.4
Alectoria-5	0.2	0.3	0.4	1.0	64.6	1510	< 0.4	297	96.4
Alectoria-6	< 0.1	< 0.24	0.4	0.9	62.5	1490	< 0.4	287	91.6
Alectoria-7	0.2	0.3	0.5	1.1	60.2	1470	< 0.4	290	92.1
Alectoria-8	0.1	< 0.24	0.3	0.9	64.7	1460	< 0.4	287	92.1
Alectoria-9	--	--	--	--	--	--	--	--	--
Alectoria-10	--	--	--	--	--	--	--	--	--
Mean	--	--	0.3	1.0	62.9	1510	< 0.4	291	94.2
SD[1]	--	--	0.1	0.1	1.7	30	--	4	2.0
RSD[2], %	--	--	46	11	3	2	--	1	2

[1]SD = Standard deviation.
[2]RSD = Relative standard deviation.
[3]All values were reported, although all results were below the UMSTRAL detection limit of 0.05%.

Table 6. Chemical analysis results for *Alectoria sarmentosa* control sample (continued).

UM lab #	Mo, µg/g	Na, µg/g	Ni, µg/g	P, µg/g	Pb, µg/g	Si, µg/g	Sr, µg/g	Ti, µg/g	V, µg/g	Zn, µg/g
Alectoria-1	< 0.2	51	< 0.4	431	5	136	7.5	4.7	< 0.4	21.0
Alectoria-2	< 0.2	49	< 0.4	419	5	152	7.5	5.2	0.8	20.4
Alectoria-3	< 0.2	48	0.5	420	6	141	7.3	4.9	0.6	20.6
Alectoria-4	< 0.2	48	< 0.4	432	5	141	7.4	4.8	0.8	20.6
Alectoria-5	< 0.2	49	0.5	433	6	154	7.4	5.3	0.6	20.9
Alectoria-6	< 0.2	49	< 0.4	419	5	154	7.3	5.0	1.9	20.2
Alectoria-7	0.2	48	0.6	423	6	125	7.2	4.5	0.7	20.1
Alectoria-8	< 0.2	50	< 0.4	416	5	155	7.0	5.0	0.5	20.1
Alectoria-9	--	--	--	--	--	--	--	--	--	--
Alectoria-10	--	--	--	--	--	--	--	--	--	--
Mean	< 0.2	49	--	424	5	145	7.3	4.9	0.7	20.5
SD[1]	--	1	--	7	0.5	11	0.2	0.3	0.5	0.3
RSD[2], %	--	2	--	2	10	8	2	5	72	2

[1]SD = Standard deviation.
[2]RSD = Relative standard deviation

analyzed on a dry-weight basis as reported in Appendix III. Elements that had more than about 25% qualified or censored values (i.e., those values below the determination limit) were excluded from statistical analysis. For elements with a very limited number of censored values, the determination limit was replaced with 0.7 times the limit (Hornung and Reed, 1990; Miesch 1976). Data means for each site were calculated as weighted averages with laboratory replicates arithmetically averaged prior to the calculation of grand means.

Many statistical techniques for data analysis require that the data distribution is normal, that is, it must follow a symmetrical bell-shaped or Gaussian curve, in order to appropriately test hypotheses or estimate probabilities. Frequently a numerical transform such as the square root or logarithm of the data is used to convert a non-normal data set to an approximately normal distribution to meet the requirements of parametric statistics. A log-transform is one of the commonly used transforms especially for dealing with environmental contaminant data (Gilbert, 1987). A variety of tests are used to evaluate the distribution of data. For example, skewness is one parameter that is used to decide whether transformation is needed (i.e., for a normal distribution the range of the skewness $\pm$ 2 * the standard error of the skewness includes zero). Based on skewness alone, many of the element concentrations for our samples appear to be right skewed and more closely resemble a lognormal distribution. However, because skewness is susceptible to strong influences of outliers, when one to three outliers are removed many of the element concentration distributions appear to be reasonably normal. Thus, in this report all statistical tests are reported for nontransformed data, but all statistical tests have also been done on log-transformed data. If transforming the

data had any effect on the statistical results and our conclusions for elements that appeared right skewed before transformation, the implications are discussed in the text.

Multivariate principal component analysis (PCA) with varimax rotation was performed for selected data. In this analysis all data were standardized (z-scored) by subtracting the mean and dividing by the standard deviation. This procedure adjusts the mean to zero and the standard deviation to one. For each PCA model the number of components was restricted to components with eigenvalues equal to or greater than one.

RESULTS AND DISCUSSION

Element Concentration Variance Among Spatial Regimes

As described in the Study Design section, a stratified systematic sampling design was used for sampling of the three lichen species in the MZW and the region. An unbalanced, hierarchical analysis of variance (ANOVA) approach was used for examining the proportion of variance attributable to the different sampling strata within MZW and within the region. Only sites that were within the subalpine zone at elevations of about 2700-3300 m were included in the ANOVA. Separate ANOVA's were performed for sites within the MZW and the region where the region was defined as all sites including sites within Routt National Forest that were outside the MZW political boundaries. A major objective of these ANOVA's was to examine whether the variance of element concentrations was attributable to differences among sites or within a site (i.e., site replication) or laboratory error. For sites within the region, another strata was included in the ANOVA to examine the proportion of variance attributable to differences among areas, such as among different wilderness areas. Because the ANOVA designs are highly unbalanced, caution must be used in interpreting the results. The ANOVA results should only be used as general indications of trends--trends that vary from element to element. Table 7 lists the number of samples that are associated with the ANOVA levels. Tables 8-10 list the percentages of total variance at each ANOVA level for separate ANOVA's that were performed for the MZW sites and the regional sites for the three lichens, *Bryoria Usnea*, and *Xanthoparmelia*. These ANOVA's were performed on nontransformed data. Log-transformation of the data prior to the ANOVA does redistribute the proportion of variance attributable to specific strata to some extent--generally in a minor fashion for most elements. However, log-transformation of the data does not impact any of our conclusions that are based on these ANOVA's.

For all lichen species the laboratory error is generally a small proportion ($<25\%$) of the total variance for most elements that were present at concentration levels significantly greater than the determination limit for the chemical analysis. In general, for two thirds or more of the elements determined in the lichens within MZW most of the variance was attributable to differences among sites and within sites. The same is true for most elements in the lichens from the regional sites, except that differences among areas also represent a fair proportion of the total variance. Because the variance attributable to differences among samples from the same general sites is greater than 25% for many elements, especially for *Xanthoparmelia* and *Usnea*, site replicates (secondary sites) have been treated as independent sites (i.e., primary sites) in all additional data analysis procedures.

Table 7. Summary of number of samples within each ANOVA level for the MZW, Regional, and Yampa Valley sampling designs.

		MZW Sampling				Regional Sampling				
Species	Measurement type[1]	Primary sites	# Site reps	# Lab reps	Total # samples	Number of areas[2]	Primary sites	# Site reps	# Lab reps	Total # Samples
Bryoria	[Element]	6	1	3	10	5	7	2	2	11
Usnea	[Element]	7	1	2	10	7	11	3	4	18
	$\delta^{34}S$	6	1	1	8	7	11	3	1	15
Xanthoparmelia	[Element]	13	3	3	19	7	14	5	4	23
	$\delta^{34}S$	10	3	1	14	7	13	3	1	17

		Yampa Valley Sampling			
Species	Measurement type[1]	Primary sites	# Site reps	# Lab reps	Total # samples
Tortula	[Element]	14	0	2	16
	$\delta^{34}S$	12	0	2	14
Xanthoria	[Element]	8	1	2	11

[1]Measurement type: Major and trace element concentration determinations ([Element]) were done on all species and stable S isotope ratios ($\delta^{34}S$) were determined on three species.
[2]Number of areas: Up to seven land management units were sampled in the Regional sampling.

For the moss (*Tortula*) and the lichen (*Xanthoria*) collected in the Yampa Valley, unbalanced hierarchical ANOVA's (Table 11) were also performed in a similar fashion to the wilderness samples described above. However, as noted in Table 7, no site replicates were collected for the moss traverse. In general, for the moss and lichen samples from the Yampa Valley the majority of the variance is attributable to differences among sites. For the *Xanthoria* samples, site replicates were treated as independent samples as was done for the other lichen species collected.

Summary Statistics for Element Concentrations

To provide a general understanding of the distribution of element concentrations in the lichen and moss samples summary statistics were calculated by species without regard to collection location. Summary statistics are presented in Tables 12-16 for element

Table 8. ANOVA results for elements in *Bryoria* for MZW and Regional sites.

	Percentage of total variance[1] at each ANOVA level									
	MZW Sites				Regional Sites					
Element	Among sites within MZW		Site replication	Lab error	Total Variance	Among areas within region		Among sites within area	Site replication	Lab error	Total Variance
Al, µg/g	72		19	8	12000	< 1		90	9 *	< 1	49000
Ash, %	96		3	< 1	0.14	< 1		94	6	< 1	0.43
B, µg/g	85		13 *	2	120	94	*	6 *	< 1	< 1	690
Ba, µg/g	49		19	32	6.7	55		39	6 *	< 1	50
Be, µg/g	-		-	-	-	-		-	-	-	-
Ca, µg/g	87		< 1	13	420000	80		4	15 *	< 1	770000
Cd, µg/g	31		< 1	69	0.0024	75		4	4	16	0.016
Cr, µg/g	96		< 1	4	0.042	< 1		84	11	5	0.1
Cu, µg/g	80		4	16	0.19	< 1		88	11 *	< 1	0.74
Fe, µg/g	74		16	10	9400	< 1		92	8 *	< 1	47000
K, µg/g	39		48	13	130000	< 1		92	8 *	< 1	290000
Li, µg/g	-		-	-	-	-		-	-	-	-
Mg, µg/g	85		< 1	15	3500	< 1		99 *	< 1	< 1	11000
Mn, µg/g	96		< 1	4	1600	74	*	< 1	26 *	< 1	1300
N, %	48		17	35	0.014	< 1		97 *	2	< 1	0.21
Na, µg/g	92		< 1	8	130	< 1		96 *	4 *	< 1	820
Ni, µg/g	96		< 1	4	0.041	< 1		73	24	2	0.097
P, µg/g	35		62 *	4	68000	< 1		62	38 *	< 1	14000
Pb, µg/g	100		< 1	< 1	1.1	< 1		79	21	< 1	6.5
S, %	64		< 1	36	0.0002	< 1		97 *	1	1	0.0021
$\delta^{34}S$, ‰	-		-	-	-	-		-	-	-	-
Si, µg/g	< 1		86	14	6500	< 1		87	10	3	23000
Sr, µg/g	90	*	< 1	10	2.7	< 1		16	84 *	< 1	9.9
Ti, µg/g	75		4	22	6.4	< 1		94	6	< 1	35
Zn, µg/g	44		30	26	8.1	74		25 *	< 1	< 1	31

[1] There is a significant difference between levels separated by an * at $p < 0.05$.

Table 9. ANOVA results for elements in *Usnea* for MZW and Regional sites.

	Percentage of total variance[1] at each ANOVA level									
	MZW Sites				Regional Sites					
Element	Among sites within MZW		Site replication		Lab error	Total Variance	Among areas within region		Among sites within area		Site replication		Lab error	Total Variance
Al, µg/g	95		3	*	2	3200	< 1		89		11	*	< 1	22000
Ash, %	< 1		96		4	0.062	65		19		14	*	2	0.37
B, µg/g	66		32	*	2	16	22		78	*	< 1		< 1	77
Ba, µg/g	26		2		71	22	12		< 1		88	*	< 1	120
Be, µg/g	-		-		-	-	-		-		-		-	-
Ca, µg/g	71		27	*	2	1100000	73	*	6		20	*	< 1	2800000
Cd, µg/g	4		< 1		96	0.0052	64		26		< 1		10	0.012
Cr, µg/g	< 1		13		87	0.058	< 1		80		3		17	0.044
Cu, µg/g	< 1		53		47	0.069	< 1		72		24	*	4	0.40
Fe, µg/g	96		< 1		4	2000	< 1		96	*	3		< 1	16000
K, µg/g	43		55	*	2	120000	28	*	< 1		72	*	< 1	940000
Li, µg/g	-		-		-	-	-		-		-		-	-
Mg, µg/g	38		61	*	1	4100	46		< 1		53	*	< 1	26000
Mn, µg/g	100	*	< 1	*	< 1	4200	35		< 1		65	*	< 1	3000
N, %	< 1		96	*	4	0.069	< 1		71		28	*	2	0.078
Na, µg/g	63		27		10	13	< 1		66		34	*	< 1	270
Ni, µg/g	55		< 1		45	0.072	< 1		80		12		8	0.062
P, µg/g	60		39	*	< 1	100000	32	*	< 1		68	*	< 1	400000
Pb, µg/g	66		< 1		34	1.5	< 1		60		36	*	3	4.0
S, %	67		26		7	0.0004	< 1		59		35	*	6	0.0011
$\delta^{34}S$, ‰	89		< 1		11	0.41	72	*	< 1		25		3	0.65
Si, µg/g	81		< 1		19	6700	< 1		74		26	*	< 1	23000
Sr, µg/g	84		16	*	< 1	8.4	68	*	< 1		32	*	< 1	40
Ti, µg/g	96	*	< 1		4	3.3	< 1		96	*	3		< 1	16
Zn, µg/g	< 1		99	*	1	6	45		46		7	*	1	24

[1] There is a significant difference between levels separated by an * at p <0.05.

Table 10. ANOVA results for elements in *Xanthoparmelia* for MZW and Regional sites.

	Percentage of total variance[1] at each ANOVA level									
	MZW Sites				Regional Sites					
Element	Among sites within MZW	Site replication	Lab error	Total Variance	Among areas within region	Among sites within area	Site replication	Lab error	Total Variance
Al, µg/g	97 *	< 1	2	600000	31	< 1	25	44	470000
Ash, %	< 1	96 *	4	12	56 *	10	2	32	21
B, µg/g	56	32	12	1.3	< 1	< 1	77	23	0.32
Ba, µg/g	< 1	96 *	3	56	40	34	20	6	180
Be, µg/g	85 *	14 *	1	0.003	21	24	5	49	0.002
Ca, µg/g	60	38 *	2	63000000	52 *	17	26 *	4	120000000
Cd, µg/g	20	72 *	8	0.4	28	40	21	11	0.12
Cr, µg/g	79	11	10	0.64	< 1	97 *	2	1	27
Cu, µg/g	63	30	7	2.1	< 1	56	39 *	6	1.1
Fe, µg/g	84	13	3	510000	55 *	< 1	11	34	900000
K, µg/g	17	78 *	5	65000	< 1	50	50 *	< 1	180000
Li, µg/g	78	22 *	< 1	0.77	44 *	6	< 1	50	0.61
Mg, µg/g	42	50	7	31000	< 1	32	55 *	12	83000
Mn, µg/g	30	68 *	1	1400	< 1	81 *	16 *	2	1600
N, %	36	29	35	0.03	< 1	54	40 *	7	0.025
Na, µg/g	98 *	< 1	1	420	37 *	< 1	53 *	10	330
Ni, µg/g	82	3	15	0.45	36 *	< 1	59 *	6	3.2
P, µg/g	71	28 *	1	45000	46	13	40 *	< 1	28000
Pb, µg/g	57	39 *	3	100	36	37	26 *	< 1	74
S, %	55	30	15	0.0002	< 1	49	37	14	0.0002
$\delta^{34}S$, ‰	80	10	10	0.2	23	21	56	< 1	0.3
Si, µg/g	< 1	38	62	7700	15	10	29	46	9500
Sr, µg/g	35	63	2	49	30	38	30 *	1	510
Ti, µg/g	< 1	97 *	3	840	36	34	24	6	1800
Zn, µg/g	31	68 *	1	72	49 *	36	13 *	1	85

[1] There is a significant difference between levels separated by an * at p <0.05.

Table 11. ANOVA results for elements in *Tortula* and *Xanthoria* in the Yampa Valley.

	Percentage of total variance[1] at each ANOVA level							
	Tortula				*Xanthoria*			
Element	Among sites		Lab error	Total Variance	Among sites	Site replication	Lab error	Total Variance
Al, µg/g	100	*	< 1	5300000	40	49	11	470000
Ash, %	99	*	< 1	72	84	16 *	< 1	7.8
B, µg/g	99	*	1	68	49	51 *	< 1	120
Ba, µg/g	100	*	< 1	740	81	19 *	< 1	340
Be, µg/g	100	*	< 1	0.017	48	38	14	0.0009
Ca, µg/g	100	*	< 1	7000000	97	2	1	3300000
Cd, µg/g	99	*	< 1	0.30	96	2	2	0.13
Cr, µg/g	100	*	< 1	4.4	39	44	17	0.67
Cu, µg/g	100	*	< 1	4.0	93	4	2	1.8
Fe, µg/g	100	*	< 1	3800000	74	21	5	560000
K, µg/g	98	*	2	460000	98	< 1	2	930000
Li, µg/g	98	*	2	1.3	50	44	6	0.36
Mg, µg/g	100	*	< 1	390000	88	11	1	320000
Mn, µg/g	100	*	< 1	1600	97	2	< 1	29000
N, %	84		16	0.021	89	9	1	0.080
Na, µg/g	99	*	< 1	450	98	1	< 1	13000
Ni, µg/g	98	*	2	8.4	81	9	10	0.43
P, µg/g	100	*	< 1	87000	91	8	< 1	190000
Pb, µg/g	92		8	14	76	21	3	8.2
S, %	80		20	0.0002	69	29	2	0.0015
$\delta^{34}S$, ‰	99	*	1	3.6	-	-	-	-
Si, µg/g	93		7	49000	30	< 1	70	24000
Sr, µg/g	100	*	< 1	190	78	21 *	< 1	110
Ti, µg/g	98	*	2	270	10	67	23	310
Zn, µg/g	97	*	3	92	62	38 *	< 1	3200

[1] There is a significant difference between levels separated by an * at p <0.05.

Table 12. Summary statistics for elements in *Bryoria* (n = 16, dry-weight basis).

Element	Minimum	Maximum	Median	Arithmetic Mean	Standard Deviation	Geometric Mean	Geometric Deviation
Al, µg/g	333	865	433	465	130	450	1.29
Ash, %	1.9	3.2	2.3	2.3	0.4	2.31	1.16
B, µg/g	16.8	78.0	29.7	36.9	18	33.4	1.57
Ba, µg/g	12.3	33.4	21.6	21.1	5.4	20.5	1.30
Be, µg/g	< 0.04	0.05	-	-	-	-	-
Ca, µg/g	1660	4260	2930	2960	680	2890	1.27
Cd, µg/g	0.2	0.6	0.3	0.3	0.1	0.29	1.34
Cr, µg/g	0.5	1.2	0.6	0.7	0.2	0.7	1.31
Cu, µg/g	2.7	4.8	3.2	3.4	0.5	3.4	1.16
Fe, µg/g	361	817	435	482	120	470	1.26
K, µg/g	2980	4050	3410	3460	310	3440	1.09
Li, µg/g	< 0.4	0.8	-	-	-	-	-
Mg, µg/g	461	694	572	571	57	569	1.11
Mn, µg/g	63.4	177	117	114	32	109	1.35
N, %	0.96	1.94	1.16	1.22	0.25	1.20	1.20
Na, µg/g	42	120	66	69	18	67	1.28
Ni, µg/g	0.6	1.3	0.8	0.8	0.2	0.8	1.27
P, µg/g	878	1550	1120	1120	180	1110	1.17
Pb, µg/g	6	11	8	7	2	7	1.21
S, %	0.12	0.25	0.15	0.16	0.03	0.15	1.18
$\delta^{34}S$, ‰[1]	-	-	-	-	-	-	-
Si, µg/g	449	804	559	581	96	574	1.17
Sr, µg/g	6.3	16.2	10.0	10.0	2.4	9.7	1.27
Ti, µg/g	9.7	23.2	12.4	13.3	3.4	12.9	1.25
Zn, µg/g	28.4	44.0	34.6	34.6	4.5	34.3	1.13

[1]Stable S isotope ratios were not determined.

Table 13. Summary statistics for elements in *Usnea* (n = 22, dry-weight basis).

Element	Minimum	Maximum	Median	Arithmetic Mean	Standard Deviation	Geometric Mean	Geometric Deviation
Al, µg/g	223	638	351	375	100	363	1.29
Ash, %	2.2	4.4	2.7	2.8	0.5	2.71	1.20
B, µg/g	3.0	28.0	5.8	8.2	6.4	6.83	1.76
Ba, µg/g	13.8	46.6	21.0	23.2	8.4	22.1	1.37
Be, µg/g	< 0.04	0.05	-	-	-	-	-
Ca, µg/g	2760	8980	5160	5270	1500	5060	1.34
Cd, µg/g	0.3	0.7	0.4	0.4	0.1	0.4	1.24
Cr, µg/g	0.5	1.0	0.6	0.6	0.1	0.6	1.22
Cu, µg/g	2.0	3.6	2.4	2.6	0.4	2.5	1.16
Fe, µg/g	155	507	258	275	80	266	1.31
K, µg/g	2870	4820	3540	3620	500	3590	1.14
Li, µg/g	< 0.4	0.6	-	-	-	-	-
Mg, µg/g	435	900	584	602	120	592	1.20
Mn, µg/g	93.0	258	144	155	48	149	1.35
N, %	0.68	1.58	0.90	0.97	0.19	0.95	1.20
Na, µg/g	52	101	60	64	13	63	1.20
Ni, µg/g	0.3	1.0	0.6	0.6	0.2	0.6	1.41
P, µg/g	707	1960	1010	1110	350	1070	1.32
Pb, µg/g	4	9	5	6	1	6	1.26
S, %	0.10	0.20	0.12	0.12	0.02	0.12	1.19
$\delta^{34}S$, ‰[1]	+5.2	+8.2	+6.7	+6.7	0.9	+6.6	1.15
Si, µg/g	404	827	568	595	120	585	1.21
Sr, µg/g	6.8	28.4	12.2	14.2	5.6	13.3	1.45
Ti, µg/g	7.4	18.6	11.3	11.3	2.4	11.1	1.22
Zn, µg/g	23.0	39.9	27.3	28.0	4.2	27.8	1.15

[1]For stable S isotope ratio: n = 21.

Table 14. Summary statistics for elements in *Xanthoparmelia* (n = 35, dry-weight basis).

Element	Minimum	Maximum	Median	Arithmetic Mean	Standard Deviation	Geometric Mean	Geometric Deviation
Al, µg/g	2000	4560	3160	3180	650	3110	1.24
Ash, %	8.5	24.6	15.9	16.3	3.9	15.8	1.28
B, µg/g	2.6	6.5	3.4	3.8	0.9	3.7	1.24
Ba, µg/g	14.7	61.3	32.2	33.6	10	32.1	1.36
Be, µg/g	0.09	0.29	0.14	0.16	0.05	0.15	1.34
Ca, µg/g	4570	36200	15300	17700	8900	15200	1.79
Cd, µg/g	0.5	1.6	0.9	0.9	0.2	0.9	1.32
Cr, µg/g	2.2	23.4	3.5	4.2	3.5	3.7	1.54
Cu, µg/g	4.4	11.9	7.1	7.4	1.4	7.3	1.20
Fe, µg/g	1910	4410	2980	3050	770	2950	1.30
K, µg/g	1670	3640	2840	2760	420	2720	1.18
Li, µg/g	1.4	4.4	2.4	2.4	0.8	2.3	1.37
Mg, µg/g	749	1960	981	1040	230	1020	1.22
Mn, µg/g	37.6	182	71.5	81.3	38	73.7	1.56
N, %	0.86	1.93	1.22	1.21	0.20	1.20	1.17
Na, µg/g	60	139	81	86	19	84	1.24
Ni, µg/g	2.1	7.9	3.3	3.5	1.2	3.3	1.34
P, µg/g	740	1710	1130	1150	210	1130	1.20
Pb, µg/g	18	57	36	34	10	32	1.35
S, %	0.08	0.18	0.12	0.12	0.02	0.11	1.18
$\delta^{34}S$, ‰[1]	+5.0	+7.2	+6.0	+6.1	0.5	+6.0	1.09
Si, µg/g	753	1230	978	979	94	974	1.10
Sr, µg/g	8.2	77.2	19.8	25.3	16	21.7	1.71
Ti, µg/g	39.4	195	78.9	87.8	37	81.5	1.47
Zn, µg/g	28.8	73.2	51.5	50.6	10	49.6	1.22

[1]For stable S isotope ratio: n = 29.

Table 15. Summary statistics for elements in *Tortula* (n = 14, dry-weight basis).

Element	Minimum	Maximum	Median	Arithmetic Mean	Standard Deviation	Geometric Mean	Geometric Deviation
Al, µg/g	1800	9470	5180	5080	669	4440	1.76
Ash, %	8.1	34.5	20.7	21.3	8.9	19.3	1.63
B, µg/g	8.4	36.6	25.3	24.0	8.2	22.5	1.50
Ba, µg/g	49.1	156	86.8	90.4	28.7	86.2	1.38
Be, µg/g	0.09	0.53	0.28	0.28	0.14	0.24	1.79
Ca, µg/g	7580	18700	10200	10600	2800	10300	1.27
Cd, µg/g	0.3	2.0	0.6	0.9	0.2	0.7	1.82
Cr, µg/g	2.2	10.1	6.0	5.8	2.2	5.3	1.54
Cu, µg/g	6.0	13.2	10.4	9.8	2.1	9.6	1.26
Fe, µg/g	1560	7990	4820	4710	2100	4200	1.71
K, µg/g	2530	4800	3700	3680	720	3610	1.22
Li, µg/g	1.4	5.9	3.3	3.1	1.2	2.9	1.50
Mg, µg/g	1310	3370	2470	2310	640	2220	1.36
Mn, µg/g	80.6	216	156	153	40	147	1.33
N, %	1.14	1.61	1.28	1.33	0.15	1.33	1.12
Na, µg/g	60	134	88	90	22	88	1.28
Ni, µg/g	2.2	12.3	6.8	6.7	3.0	6.0	1.68
P, µg/g	1300	2470	1820	1820	310	1800	1.19
Pb, µg/g	6	21	9	10	4	10	1.37
S, %	0.15	0.20	0.16	0.17	0.02	0.17	1.10
$\delta^{34}S$, ‰[1]	+0.6	+6.8	+5.0	+4.2	2.0	+3.6	2.03
Si, µg/g	332	1280	1100	1000	230	964	1.39
Sr, µg/g	28.7	69.0	44.8	47.7	13	46.0	1.32
Ti, µg/g	32.8	98.6	58.2	59.5	17	57.2	1.34
Zn, µg/g	22.6	54.2	45.2	42.4	9.9	41.2	1.30

[1]For stable S isotope ratio: n = 12.

Table 16. Summary statistics for elements in *Xanthoria* (n = 9, dry-weight basis).

Element	Minimum	Maximum	Median	Arithmetic Mean	Standard Deviation	Geometric Mean	Geometric Deviation
Al, µg/g	1940	4530	3110	3130	730	3060	1.27
Ash, %	8.8	17.1	11.3	12.7	2.9	12.4	1.26
B, µg/g	16.9	46.7	39.0	34.0	11	32.0	1.46
Ba, µg/g	31.0	103	49.3	53.2	20	50.6	1.38
Be, µg/g	0.09	0.19	0.14	0.14	0.03	0.14	1.25
Ca, µg/g	4240	9760	4680	5860	1900	5620	1.35
Cd, µg/g	0.6	1.7	1.3	1.2	0.3	1.2	1.37
Cr, µg/g	2.2	5.3	3.5	3.6	0.9	3.5	1.28
Cu, µg/g	5.9	9.8	7.3	7.6	1.4	7.5	1.20
Fe, µg/g	1490	4230	2420	2620	790	2510	1.35
K, µg/g	8040	10600	9850	9500	870	9460	1.10
Li, µg/g	1.8	4.0	2.7	2.8	0.6	2.8	1.26
Mg, µg/g	1940	3560	2340	2480	560	2430	1.24
Mn, µg/g	48.1	626	88.4	150	61	105	2.18
N, %	1.65	2.71	2.05	2.11	0.30	2.09	1.15
Na, µg/g	89	440	137	185	120	159	1.73
Ni, µg/g	2.2	4.5	3.3	3.1	0.7	3.1	1.24
P, µg/g	2230	3720	2750	2830	440	2800	1.16
Pb, µg/g	7	16	12	11	3	11	1.30
S, %	0.29	0.42	0.34	0.35	0.04	0.35	1.12
$\delta^{34}S$, ‰[1]	-	-	-	-	-	-	-
Si, µg/g	919	1390	1110	1100	140	1090	1.13
Sr, µg/g	23.9	60.6	34.0	36.3	11	35.0	1.33
Ti, µg/g	45.0	114	70.4	74.6	19	72.5	1.29
Zn, µg/g	76.0	232	172	166	52	158	1.43

[1]Stable S isotope ratios were not determined.

Table 17. Arithmetic mean element concentrations in lichens at MZW and Regional sites[1].

	Bryoria mean concentration[2]		*Usnea* mean concentration		*Xanthoparmelia* mean concentration	
	MZW	Regional	MZW	Regional	MZW	Regional
Al, µg/g	418 ± 95	502 ± 154	307 ± 55	413 ± 104	3310 ± 750	3060 ± 550
Ash, %	2.26 ± 0.34	2.39 ± 0.37	2.48 ± 0.25	2.91 ± 0.60	16.4 ± 3.2	16.1 ± 4.4
B, µg/g	42 ± 10	33 ± 22	8.6 ± 3.4	8.0 ± 7.8	4.2 ± 1.1	3.4 ± 0.5
Ba, µg/g	19 ± 3	23 ± 7	20 ± 4	25 ± 10	33 ± 8	34 ± 13
Be, µg/g	--	--	--	--	0.17 ± 0.06	0.15 ± 0.04
Ca, µg/g	3010 ± 540	2930 ± 800	4560 ± 1040	5670 ± 1650	17200 ± 7300	18100 ± 10200
Cd, µg/g	0.3 ± 0.05	0.3 ± 0.1	0.4 ± 0.05	0.4 ± 0.1	0.9 ± 0.2	0.9 ± 0.3
Cr, µg/g	0.7 ± 0.2	0.8 ± 0.2	0.6 ± 0.1	0.7 ± 0.1	3.5 ± 0.8	3.8 ± 1.3
Cu, µg/g	3.1 ± 0.4	3.6 ± 0.5	2.3 ± 0.2	2.7 ± 0.4	8.2 ± 1.5	6.8 ± 1.0
Fe, µg/g	444 ± 87	512 ± 150	222 ± 42	306 ± 80	3110 ± 720	3000 ± 830
K, µg/g	3410 ± 350	3490 ± 300	3580 ± 350	3650 ± 570	3000 ± 270	2560 ± 430
Li, µg/g	--	--	--	--	2.7 ± 0.9	2.3 ± 0.7
Mg, µg/g	547 ± 54	590 ± 56	551 ± 64	631 ± 130	1030 ± 180	1050 ± 270
Mn, µg/g	120 ± 35	109 ± 31	164 ± 61	151 ± 40	86 ± 40	78 ± 36
N, %	1.09 ± 0.11	1.33 ± 0.28	0.87 ± 0.11	1.03 ± 0.20	1.35 ± 0.18	1.10 ± 0.14
Na, µg/g	58 ± 11	77 ± 18	55 ± 4	69 ± 14	97 ± 20	78 ± 14
Ni, µg/g	0.8 ± 0.2	0.8 ± 0.2	0.6 ± 0.2	0.6 ± 0.2	3.3 ± 0.7	3.6 ± 1.5
P, µg/g	1160 ± 260	1100 ± 100	1200 ± 340	1060 ± 350	1250 ± 220	1060 ± 160
Pb, µg/g	7.0 ± 1.0	7.7 ± 1.8	5.5 ± 1.2	6.1 ± 1.5	37 ± 10	32 ± 9
S, %	0.14 ± 0.01	0.17 ± 0.03	0.11 ± 0.02	0.13 ± 0.02	0.13 ± 0.02	0.10 ± 0.01
$\delta^{34}S$, ‰	--	--	7.5 ± 0.6	6.3 ± 0.8	6.3 ± 0.5	5.8 ± 0.5
Si, µg/g	524 ± 68	625 ± 93	514 ± 74	642 ± 110	943 ± 85	1010 ± 94
Sr, µg/g	8.8 ± 1.5	11 ± 2.7	11 ± 3	16 ± 6	21 ± 6	29 ± 21
Ti, µg/g	12 ± 2	14 ± 4	9.9 ± 1.8	12 ± 2	86 ± 29	89 ± 43
Zn, µg/g	33 ± 3	36 ± 5	27 ± 2	29 ± 5	55 ± 9	47 ± 9

[1] Regional sites represent all samples not collected within MZW boundaries.
[2] Mean ± 1 standard deviation.

concentrations in the five species collected in the subalpine and valley terrains. Laboratory replicate analyses and blind sample replicates were arithmetically averaged prior to the calculation of the summary statistics presented in these tables. Also, as noted above, sample site replicates were treated as independent sites for these calculations. The observed range, median, arithmetic mean and standard deviation, and the geometric mean and deviation are listed for each element. If a large proportion of the samples were below the determination limit, only the observed range is given. For the lichens collected in the subalpine zone, the samples from MZW and the region were lumped together for the calculations. For many elements there are not large relative differences among the various measures of central tendency, the median and the arithmetic and geometric means. When there are large differences, high concentration values for one to three samples are typically responsible.

Trace Element Trends in MZW and Regional Samples

One of our hypotheses is that if there is substantial influence from coal combustion emissions on lichens in MZW, then element concentrations would be higher in lichens in and near MZW compared to sites more distant from and/or not downwind of the power stations. Table 17 lists the arithmetic mean concentration for elements in lichens from MZW and from all regional sites outside the MZW boundaries. Most elements in the epiphytic lichens, *Bryoria* and *Usnea*, appear to have higher average concentrations at the regional sites (Figure 12)(statistical significance of the differences is addressed below). However, B, Mn, and P were higher in MZW samples for both lichens. Stable S isotope ratios were also noticeably heavier (i.e., more positive) in MZW samples of *Usnea* which implies a likely difference in atmospheric source of S. The elevated concentrations of B, Mn, and P may represent increased deposition owing to potential coal combustion emissions. It seems unlikely that the higher concentrations reflect natural eolian dust contamination, because the ash content and many of the lithophilic elements (e.g., Al, Be, Fe, K, Li, Mn, and Na are elements that typically occur with silicates) appear higher at the regional sites.

The higher precipitation in MZW compared to most regional sites may have an influence on leaching or washing the surface of the lichen such that it would reduce the relative concentration of the elements in MZW. Elements may also be lower in MZW lichens because of leaching by higher acidity precipitation in MZW compared to regional sites. Potentially, elements, such as S, may neither increase nor decrease, but simply reach an isotopic equilibrium.

In the *Xanthoparmelia* samples, the ash content and concentrations of many of the lithophilic elements appear to be slightly higher in MZW samples compared to the regional site average (Figure 12). As seen for the epiphytic lichens, average concentrations of B, Mn, P, and S isotope ratios also appear higher in MZW samples. In addition, N and S and a few trace elements, Cu, Pb, and Zn, appear to average higher in MZW samples. Natural eolian or anthropogenic surface contaminants may account for the increased concentration in the MZW *Xanthoparmelia* samples. In this case the higher snowfall may actually help concentrate the particles on the surface of the lichen. However, increased particulate contaminants seem unlikely to entirely account for higher N and S levels in MZW. Gaseous or solution deposition are more probable.

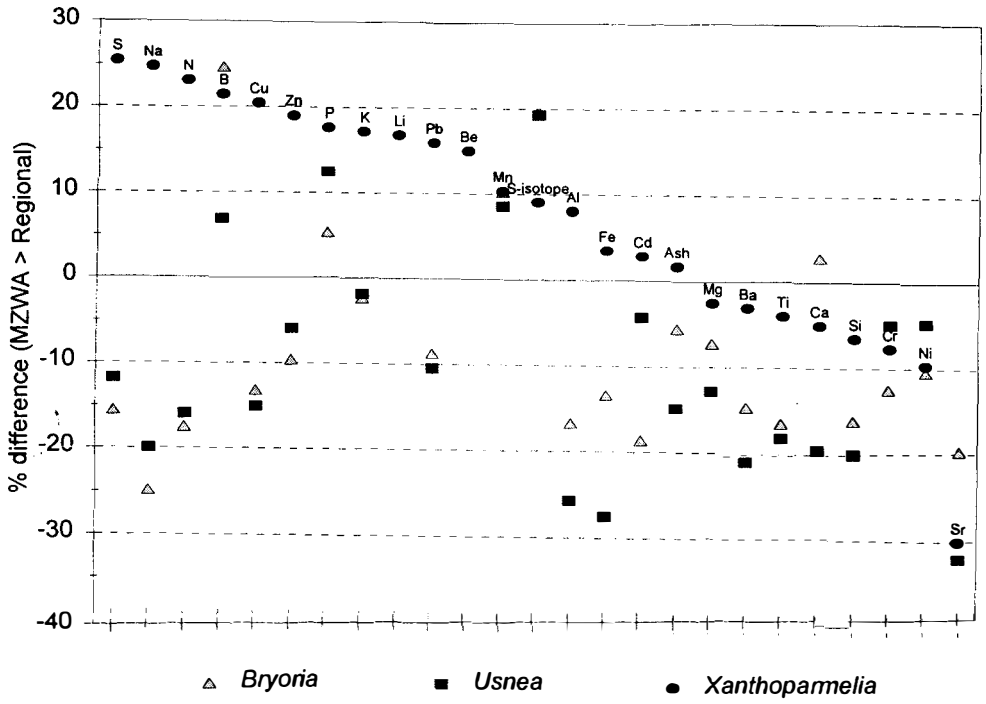

Figure 12. Relative difference in element concentration means for MZW and Regional samples of *Bryoria*, *Usnea*, and *Xanthoparmelia*.

A two-sample *t* test was used to compare the mean element concentrations in lichen samples from MZW with regional samples to evaluate which of the differences noted above are statistically significant. The same *t* test was also used to compare all sites within about 60 km of the Hayden Power Station with the remaining regional samples that averaged about 125 km from the power station. The group of sites within 60 km of Hayden was comprised of all sites within MZW, Routt National Forest, and the Flat Tops Wilderness. This latter comparison does not restrict the element concentration comparisons to just the political boundaries of MZW, but it does group the sites in the Flat Tops Wilderness that are upwind of the power stations with the MZW and Routt sites that are downwind. Because the element concentration variance within the comparison groups was not always equal, a technique which takes the separate variances into account and reduces the number of degrees of freedom was used (thus, making it harder to detect differences by decreasing the effective sample size). A Bonferroni adjustment (Kleinbaum and others, 1988) was made to the probability estimate to take into account the multiple testing of the 24 element concentrations and the stable sulfur isotope ratio. This correction increases the *p*-value by a multiple of the number of tests ($p_{corr} = n*p$, where n equals the number of variables examined). Because of the exploratory nature of this work, for each of the lichen species, the elements for which there is a difference between the sampling areas with at least a 75% confidence level

Table 18. Two-sample *t* test results for comparison of MZW versus Regional sites and sites ≤60 km versus sites ≥100 km from the Hayden Power Station (only elements with one or more comparisons significant at p <0.25).

Species	Element	MZW mean[1]	Regional mean	*p*-value, Probability[2]	≤60 km mean	≥100 km mean	*p*-value, Probability
Bryoria	B, µg/g	41.6 ± 10.4	33.3 ± 22.0	1	48.2 ± 16.3	22.4 ± 2.8	**0.025***
Usnea	Al, µg/g	307 ± 55	413 ± 104	0.13	359 ± 107	398 ± 95	1
	Cu, µg/g	2.3 ± 0.2	2.7 ± 0.4	0.20	2.5 ± 0.4	2.7 ± 0.4	1
	Fe, µg/g	222 ± 42	306 ± 80	0.10	263 ± 87	294 ± 68	1
	Na, µg/g	55 ± 4	69 ± 14	0.10	61 ± 12	68 ± 14	1
	$\delta^{34}S$, ‰	7.5 ± 0.6	6.3 ± 0.8	**0.025***	7.2 ± 0.7	6.0 ± 0.6	**0.025***
	Si, µg/g	514 ± 74	641 ± 110	0.13	571 ± 118	630 ± 113	1
Xanthoparmelia	B, µg/g	4.2 ± 1.1	3.4 ± 0.5	0.58	4.0 ± 1.0	3.3 ± 0.4	0.15
	Cu, µg/g	8.2 ± 1.5	6.8 ± 1.0	0.10	7.9 ± 1.4	6.7 ± 1.0	0.22
	K, µg/g	3000 ± 270	2560 ± 430	**0.025***	2960 ± 320	2460 ± 400	**0.025***
	N, %	1.35 ± 0.18	1.10 ± 0.14	**0.003***	1.32 ± 0.19	1.06 ± 0.11	**0.0003***
	Na, µg/g	97 ± 20	78 ± 14	0.10	95 ± 20	73 ± 8	**0.002***
	P, µg/g	1250 ± 220	1060 ± 160	0.22	1230 ± 220	1030 ± 140	**0.05***
	S, %	0.13 ± 0.02	0.10 ± 0.01	**0.0002***	0.13 ± 0.02	0.10 ± 0.01	**0.0001***
	$\delta^{34}S$, ‰	6.3 ± 0.5	5.8 ± 0.5	0.15	6.3 ± 0.4	5.7 ± 0.5	0.15
	Zn, µg/g	55.4 ± 9.0	46.5 ± 8.7	0.15	52.6 ± 10.3	47.6 ± 8.3	1

[1] Mean ± 1 standard deviation.
[2] Probablity *p*-value has been adjusted for multiple tests; * Areas are significantly different at p <0.05.

($p < 0.25$) are listed in Table 18 along with the group means for the different areas. Elements with group means that are significantly different at a much higher confidence level ($p < 0.05$) are also indicated in the table.

For *Xanthoparmelia*, K, N, and S concentrations were significantly higher ($p < 0.05$) in MZW samples compared to regional samples (log-transformation increased the probability that these concentrations were significantly different). This was also true when the MZW samples were combined with the other regional sites that were within 60 km of the Hayden Power Station and compared against all other regional sites that were greater than 100 km from the station. For this latter comparison, Na and P were also significantly higher at the sites closer to the power station. Concentrations of several other elements, Cu, Zn, and the

stable S isotope ratio, appear to be higher in the MZW samples versus the regional samples, but at a lower confidence level ($p < 0.15$-0.2). Removal of the sample with the highest concentration from the data set for these elements does not change our general conclusions regarding the significant difference in element concentrations. Thus, these differences do not appear to be the result of just an outlier sample falling within the MZW group.

For the epiphytic lichens only the stable S isotope ratio in *Usnea* and the B concentration in *Bryoria* were significantly higher ($p < 0.05$) in the MZW and/or the <60 km sites compared to the more distant regional sites. Several metals in the *Usnea* samples, Al, Cu, Fe, Na, and Si, appear to be higher at the regional sites compared to the MZW sites, but not when the sites are compared between those that are <60 km and >100 km from the power station. In this instance, removal of the two highest concentration sites (6-01 and 7-01) for Al and Si from the data set decreases the probability (i.e., $p < 0.40$) that the concentrations of these elements are truly different between the MZW and the region, but instead the difference is an artifact induced by high samples within each group that may be more contaminated with airborne dust. The probability that Fe and Na may be different between the groups is also reduced ($p < 0.25$).

Although our objective is to compare MZW with other regional sites as a group, in order to further understand why element concentrations at MZW sites may be different from regional sites, ANOVA has been used to examine differences among MZW and the seven subgroup areas within the regional sites. ANOVA with post hoc Tukey-Kramer Honestly Significant Difference (HSD) pairwise comparisons of means was used to determine which pairs of areas were significantly different. It should be noted that the Tukey HSD is a conservative test that protects against the overestimate of significant mean differences due to multiple comparisons. Although the ANOVA and pairwise test methods used handle unbalanced designs correctly, caution should be used in interpreting these results because areas within the region are only represented by 1-4 samples compared with 7-16 samples from MZW (depending upon which species). The results for selected elements and stable S isotope ratios that had a high probability of being different between the MZW and regional sites (cf. Table 18) are shown in Table 19. ANOVA indicated that for all of the elements listed in Table 19 that there was a significant difference ($p < 0.05$) among the eight areas. In Table 19 any two areas that are not underscored by the same line are considered different, but at a relatively low probability level ($p < 0.25$).

The concentrations of K, N, P, and S in *Xanthoparmelia* are consistently higher in MZW samples and significantly different from samples in Maroon Bells Wilderness and Rocky Mountain National Park (the probability that these areas are different from MZW increases if the data are log-transformed). Medicine Bow National Forest samples were different from MZW samples for K and S also. The greatest difference in stable S isotope ratios in *Xanthoparmelia* was found between MZW and Medicine Bow National Forest samples. For *Usnea* the stable S isotope ratios were most similar among the MZW, the southern Routt National Forest, and the Rocky Mountain National Park samples. MZW samples were significantly different ($p < 0.05$) than all other areas. In general, the areas that are most different from MZW are 100-150 km from the Hayden Power Station, however, not all areas at these larger distances are highly significantly different from MZW.

Table 19. Post hoc pairwise comparisons for element concentration and stable S isotope ratio differences among areas.[1,2]

Species	Element	Areas
Bryoria	B	ENW RW MBNF RMNP MZW RNF*
Usnea	$\delta^{34}S$	MBW* ENW* MBNF* FTW* RW* RMNP RNF MZW
Xanthoparmelia	K	MBNF RMNP* MBW* FTW RW ENW MZW RNF
	N	MBW RMNP MBNF RW ENW FTW RNF MZW
	Na	RMNP ENW RW RNF MBW MBNF FTW MZW
	P	MBW RMNP FTW MBNF RW ENW RNF MZW
	S	RMNP* MBW* MBNF RW FTW ENW RNF MZW
	$\delta^{34}S$	MBNF ENW FTW MBW RMNP RW RNF MZW

[1] Areas: Eagles Nest Wilderness (ENW), Flat Tops Wilderness (FTW), Medicine Bow National Forest (MBNF), Maroon Bells Wilderness (MBW), Mount Zirkel Wilderness (MZW), Rocky Mountain National Park (RMNP), Routt National Forest (RNF), and Rawah Wilderness (RW).

[2] Areas not unscored by the same line are weakly significantly different ($p < 0.25$). Areas that are significantly different ($p < 0.05$) from MZW are indicated with an asterisk. Areas are ordered approximately from lowest to highest mean concentration.

Mercury in *Xanthoparmelia*. In a previous study, in the summer of 1993, fourteen *Xanthoparmelia cumberlandia* samples were collected for the USFS (Appendix V). Eight of the samples were from Buffalo Pass near the southern boundary of MZW and one sample was from near Fish Creek Reservoir, just south of Buffalo Pass. The remaining samples were from Rocky Mountain National Park, Arapaho National Forest, and White River National Forest. The samples were analyzed for major and trace elements (see methods in Jackson and others, 1995). Mercury was determined in this suite of samples, but was not measured in samples from this study. The nine *Xanthoparmelia* samples from the Buffalo Pass area ranged from 0.13 to 0.21 μg/g Hg with a mean of 0.18 $\pm$ 0.03 μg/g, whereas the five samples from the other regional sites ranged from 0.11 to 0.12 μg/g with a mean of 0.11 $\pm$ 0.004 μg/g. At uncontaminated sites in other parts of the world, the average Hg concentration in grains and other foodstuffs is typically 0.01-0.02 μg/g (Kabata-Pendias and

Pendias, 1992). Concentrations in lichens and mosses have not been routinely measured. The relatively large difference in Hg concentration between the Buffalo Pass samples and the other regional samples suggest that there is a local source of Hg. Mercury is a volatile element that is emitted during coal combustion (Adriano, 1986). Although the higher Hg concentrations occur at a location where we have found other potentially coal-combustion related elements to be elevated, these very limited data need further investigation prior to drawing any conclusions related to the source of Hg.

Inter-element Relationships in the Lichens and Moss

Inter-element relationships in biological material frequently reflect some overriding or controlling factor that is conceptually meaningful such as may be related to nutrient processes, contamination from a unique source, or chemically similar behavior of elements that are alike in charge and size. We have used exploratory principal component analysis (PCA) as a multivariate data analysis tool to help find conceptually meaningful factors that would help explain the differences in chemical content of the vegetation sampled in this study. Our objective was to obtain a "simple structure" of easily interpretable components that explained a large proportion of the total variance and that would help explain the spatial variability of the elements. We have developed models for the five species collected that have 4-6 components and explain 83-94% of the total variance. The models and the component loadings for each element are listed in Tables 20-24. Those elements that have high loadings on an individual component are the elements that are highly correlated with each other in multidimensional space. A component loading of 0.5 indicates that the component accounts for 25% of the variance of an element, whereas a loading of 0.9 accounts for 81% of the variance. Positive and negative loadings are arbitrarily assigned and only represent inter-element relationships within a component, not absolute concentrations.

The component loadings and the standardized data for each sample have been used to calculate principal component scores for the sites for each PCA model. The component scores have been plotted versus location in order to better understand the spatial distribution of elements within the study area. A two-sample *t* test was used to compare component scores between MZW sites and regional sites as was done for individual elements discussed above. The *t* test was also performed to compare component scores for sites within 60 km of the Hayden Power station against all more distant regional sites. A Bonferroni adjustment was made to the probability values for the multiple component score comparisons as above.

PCA models for *Bryoria* and *Usnea* are relatively similar (Tables 20 and 21). The major principal component (PC I) is composed of high loadings for Al, Fe, Si, Ti, and a variety of other trace elements that are typically associated as components of alumino-silicate minerals and that may be attributed, at least in part, to dust contamination of the lichen thalli. Several of the elements, such as Cu and Fe are also important micronutrients. Two other nutrients, N and S, also load highly on this component. Although this component may appear to be associated with dust contamination of the lichen, the relationship of N and S to the silicate-forming elements is unclear. This loading on the same component may indicate that the elements are not necessarily from the same source, but instead are related because of a process such as solubilization and uptake due to rainfall or removal through better washing

Table 20. Varimax rotated component loadings for elements in *Bryoria* for MZW and Regional sites.

	Component Loadings ≥ 0.50				
Element	Component I	Component II	Component III	Component IV	Component V
Al	0.97				
Ash	0.76				
B		-0.73			
Ba		0.72			0.51
Ca		0.57			0.58
Cd				0.93	
Cr	0.89				
Cu	0.93				
Fe	0.96				
K	0.63		0.72		
Mg	0.69				
Mn					0.90
N	0.89				
Na	0.92				
Ni	0.90				
P			0.94		
Pb	0.77				
S	0.97				
Si	0.94				
Sr		0.90			
Ti	0.98				
Zn				0.75	
Eigenvalue	11.2	2.5	2.4	2.0	1.8
% of total variance	51.1	11.6	11.1	9.1	8.3
Cumulative % variance	51.1	62.7	73.8	82.9	91.2

Table 21. Varimax rotated component loadings for elements in *Usnea* for MZW and Regional sites.

	Component Loadings ≥ 0.50				
Element	Component I	Component II	Component III	Component IV	Component V
Al	0.96				
Ash		0.67			
B		-0.69			
Ba		0.77			
Ca		0.88			
Cd					0.94
Cr	0.68			0.53	
Cu	0.84				
Fe	0.97				
K			0.92		
Mg			0.64		
Mn				-0.82	
N	0.76				
Na	0.80				
Ni				0.88	
P			0.95		
Pb	0.70				
S	0.84				
$\delta^{34}S$		-0.80			
Si	0.90				
Sr		0.80			
Ti	0.94				
Zn					0.85
Eigenvalue	8.0	4.3	3.0	2.2	1.9
% of total variance	35.0	18.7	13.0	9.6	8.4
Cumulative % variance	35.0	53.7	66.7	76.3	84.7

Table 22. Varimax rotated component loadings for elements in *Xanthoparmelia* for MZW and Regional sites.

	Component Loadings ≥ 0.50					
Element	Component I	Component II	Component III	Component IV	Component V	Component VI
Al		0.65	0.50			
Ash		0.75				
B	0.73	0.50				
Ba					0.82	
Be		0.83				
Ca				0.92		
Cd				0.80		
Cr			0.77			
Cu	0.68					
Fe		0.59	0.72			
K	0.85					
Li		0.81				
Mg			0.82			
Mn	0.51					
N	0.83					
Na	0.66				-0.51	
Ni			0.93			
P	0.91					
Pb					-0.62	
S	0.91					
$\delta^{34}S$						0.85
Si					0.48*	
Sr				0.91		
Ti			0.69			
Zn	0.74					
Eigenvalue	6.0	4.0	3.9	3.2	2.5	1.1
% of total variance	24.1	15.8	15.7	12.8	9.9	4.6
Cumulative % variance	24.1	39.9	55.6	68.4	78.3	82.9

* Highest loading for Si on any component.

Table 23. Varimax rotated component loadings for elements in *Tortula* for Yampa Valley sites.

	Component Loadings ≥ 0.50				
Element	Component I	Component II	Component III	Component IV	Component V
Al	0.96				
Ash	0.96				
B	0.72				0.58
Ba					0.84
Be	0.94				
Ca			0.71		
Cd		0.86			
Cr	0.97				
Cu	0.83				
Fe	0.94				
K			-0.91		
Li	0.95				
Mg	0.90				
Mn		-0.78			
N				-0.80	
Na	0.97				
Ni	0.69	0.56			
P			-0.84		
Pb	0.70				
S				-0.95	
$\delta^{34}S$		-0.93			
Si	0.57				
Sr					0.50
Ti				-0.60	
Zn			0.56		
Eigenvalue	10.7	3.3	3.3	2.8	2.3
% of total variance	42.8	13.4	13.3	11.2	9.1
Cumulative % variance	42.8	56.2	69.5	80.7	89.8

Table 24. Varimax rotated component loadings for elements in *Xanthoria* for Yampa Valley sites.

	Component Loadings ≥ 0.50			
Element	Component I	Component II	Component III	Component IV
Al	0.94			
Ash	0.76	0.60		
B				-0.91
Ba	0.93			
Be	0.87			
Ca	0.78			0.54
Cd		0.51	0.71	
Cr	0.96			
Cu	0.80			
Fe	0.95			
K			0.71	
Li	0.92			
Mg	0.76		0.50	
Mn		0.82		0.51
N		0.75		-0.53
Na		0.94		
Ni	0.97			
P		0.92		
Pb			-0.52	-0.62
S		0.71		
Si	0.76			
Sr		0.90		
Ti	0.92			
Zn			0.84	
Eigenvalue	10.8	6.0	2.8	2.8
% of total variance	45.0	25.1	11.8	11.6
Cumulative % variance	45.0	70.1	81.9	93.5

or leaching of the elements by higher rainfall. It may be that the latter process is fairly important because the average concentration of many of these elements (except N and S) is lower in the high rainfall MZW compared to the regional sites. Principal component scores versus location are shown in Figures 13 and 14 for the two lichens. The PC I score plot (Figure 14) for *Usnea* gives some indication that component scores are different between MZW and the regional sites. A *t* test indicated that the PC I scores for the areas were statistically different ($p < 0.1$).

PC II for both species has three divalent alkaline earth elements (Ba, Ca, Sr) that are inversely related to B. Calcium is a macronutrient that Sr and Ba, to some extent, tend to mimic because of similar chemical properties. Calcium and B have been noted as having antagonistic interaction in vascular plants (Adriano, 1986). Coal combustion is a major anthropogenic source of B (Adriano, 1986; Anderson and others, 1994) and also has been observed as a source of Sr (Gough and Erdman, 1977; Straughan and others, 1981). Stable S isotope ratios were determined in *Usnea* and loaded inversely on this component. PC II scores *Usnea* indicate the distinct differences in the MZW and southern Routt National Forest samples compared to the other samples in the region. These differences are generally due to higher stable S isotope ratios and B concentrations and lower Ca and Sr concentrations in MZW and Routt samples compared to the other regional samples. The PC II scores for *Unea* are statistically different ($p < 0.10$) for MZW versus the other regional sites. When scores for the southern Routt National Forest samples are grouped with the MZW samples versus all other regional sites the difference is significant at a much greater probability ($p < 0.01$) (Figure 14).

The third component of the PCA models appears to be related to nutrient status of K and P (and Mg for *Usnea*) with no clearly identifiable regional trends. Conceptually meaningful component labels and identifiable regional trends are not obvious for the last two components of the models, although both models do have a component that is strongly influenced by Cd and Zn.

Principal component V for *Bryoria* has a high loading for Mn, one of numerous elements that coal combustion contributes to the atmosphere (Adriano, 1986), and moderate loadings for Ba and Ca. Manganese, Ba, and Ca concentrations in *Bryoria* are slightly higher, although not by a statistically significant amounts, in samples from MZW and southern Routt National Forest compared to the regional sites at greater than 60 km from the Hayden Power station. However, a *t* test indicates that PC V component scores are statistically different ($p < 0.05$) for sites less than 60 km from the power station versus more distant sites (Figure 13). These results indicate the complexity of understanding some of the inter-element associations.

Table 22 lists the component loadings for the PCA model for the lichen *Xanthoparmelia* that grows on a rock substrate. The model is somewhat different than the *Usnea* and *Bryoria* models. The major component (PC I) has many nutrient elements, B, Cu, K, Mn, N, P, S, and Zn, loaded on it, but this component only accounts for 24% of the total variance compared to 35-51% for PC I in the previous models. The plot of PC I scores versus location indicates that the MZW and most of the sites in the southern Routt National Forest are considerably different than most of the regional sites (Figure 15). A large portion of this difference appears to be due to the higher concentrations of N, K, P, and S in the

MZW. A t test of PC I scores for sites less than 60 km from the Hayden Power station versus more distant regional sites indicated a statistically significant difference ($p < 0.05$) between scores.

The second and third components have many of the alumino-silicate associated elements. The separation into two components may be partly a reflection of differences in the chemistry of dust, substrate, or other surface contaminants for the rock-growing lichen, whereas the epiphytic lichens had a much lower ash content along with a much different growth form which would make it more difficult to detect potential differences in the chemistry of surface contaminants. For example, Be and Li were not included in the *Usnea* and *Bryoria* models because they were generally below the limit of determination. PC III shows the strong association of Ca and Sr as in the previous models, but Cd is included in this model along with Ca and Sr. The fifth component with Ba inversely related to Pb and Na is also different from the previous models. None of these components (PC II-V) shows any obvious regional trends (based on score plots and t tests). The last component has only stable S isotope ratios loaded highly on it in contrast to being associated with B and the alkaline earth elements in the *Usnea* model. The component score plot illustrates the generally higher isotope ratios that are found in or near MZW. This is more well defined in a section below where only the isotope ratios are plotted and not the component scores which are influenced to some extent by all elements in the model. Results of a t test for MZW and other sites less than 60 km from the Hayden stations versus more distant regional sites indicated a statistically significant difference ($p = 0.08$) in PC VI scores. If Flat Tops Wilderness samples are grouped with the more distant sites the probability of significant difference between areas increases slightly (i.e., $p < 0.05$).

The PCA models for the two Yampa Valley species are relatively similar to each other and to the models discussed above in that the major component that accounts for 42-45% of the total variance is highly loaded with Al, Fe, and a variety of other metals (Tables 23-24). As noted previously these associations suggest that a large proportion of the variability of these elements in the Yampa Valley moss and lichen is influenced by dust, soil, or possibly bark contamination.

Stable S isotope ratios were determined in *Tortula* and in the PCA model appear to be associated with Mn levels and inversely associated with Cd and Ni. The reason for these associations is unclear. As in the previous models, N and S generally load highly on the same component, but S concentration and isotope ratios do not seem to be strongly related. Although there are some similarities among the remaining components in these two PCA models and the previous models, conceptually meaningful component labels are not obvious, but nutrient relationships appear to have some influence on the component associations. Distinct spatial trends within the valley for the component scores (Figures 16 and 17) are also not readily obvious (this is discussed more fully in another section below).

In the exploratory PCA a search for simpler structure through different forms of component rotation or removal of potential nuisance variables has not been done. Several points seem evident despite the complexity of the interelement relationships in the species sampled and the difficulties in assigning conceptually meaningful labels. Regional trends for most elements are ambiguous and may be obscured by dust and soil or rock and bark substrate contamination of the samples. High Fe and Al containing fly ash contamination of

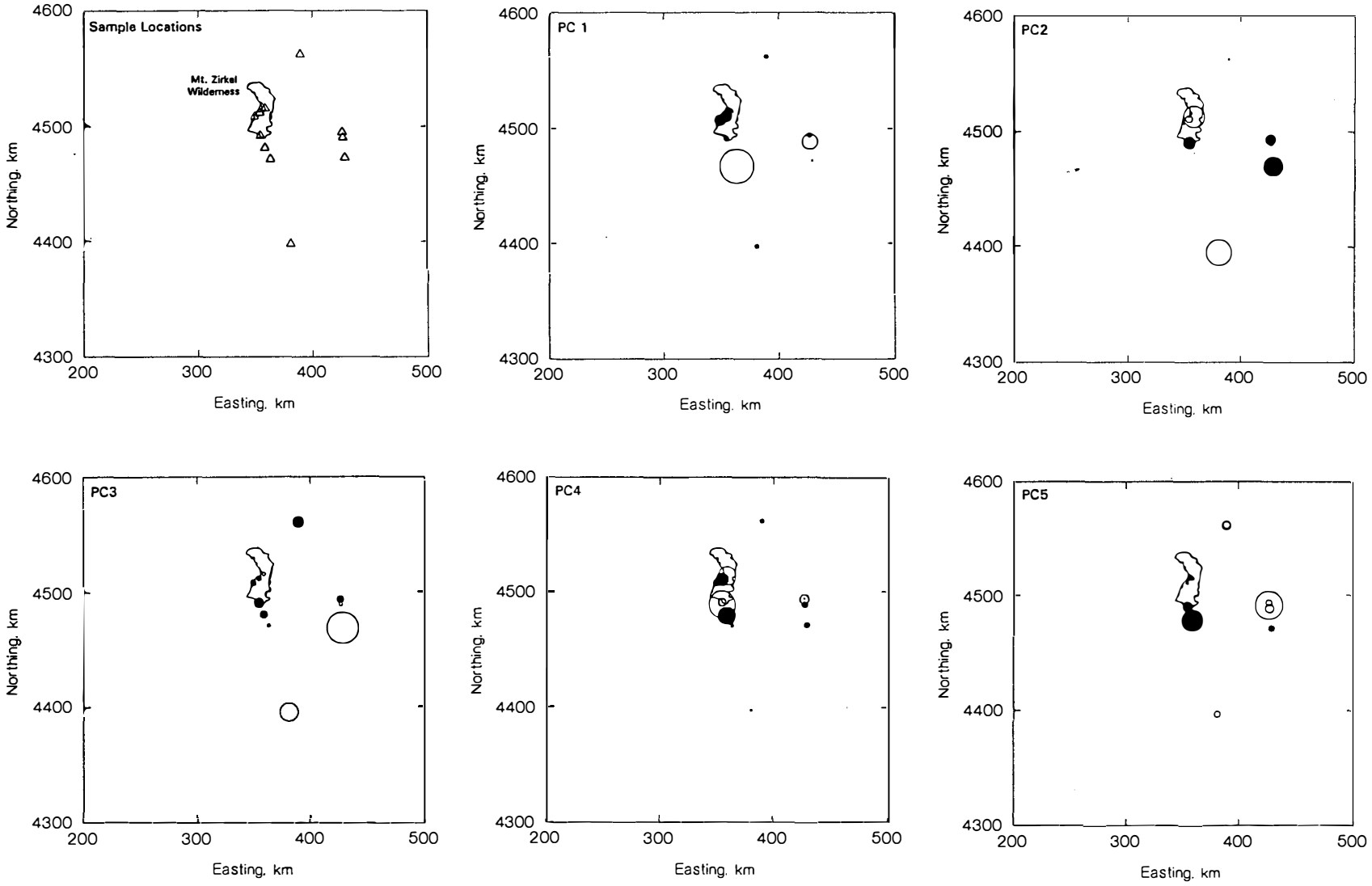

Figure 13. Principal component scores for *Bryoria* versus location. Circle diameter is proportional to standardized component score (i.e., mean score = 0 and standard deviation = 1, the greater the deviation from the mean the greater the diameter). Open circles have a positive score and filled circles have a negative score.

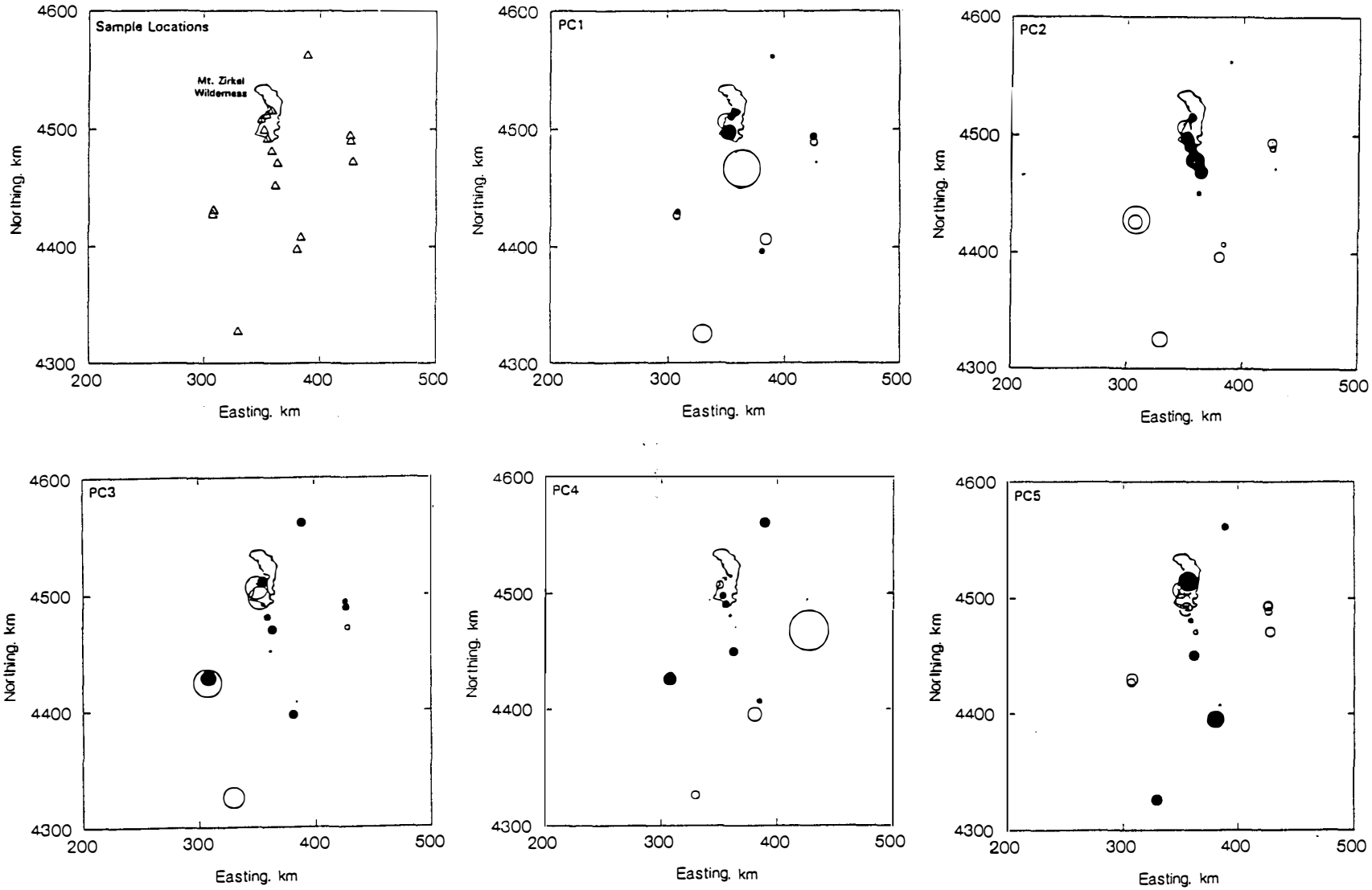

Figure 14. Principal component scores for *Usnea* versus location. Circle diameter is proportional to standardized component score (i.e., mean score = 0 and standard deviation = 1, the greater the deviation from the mean the greater the diameter). Open circles have a positive score and filled circles have a negative score.

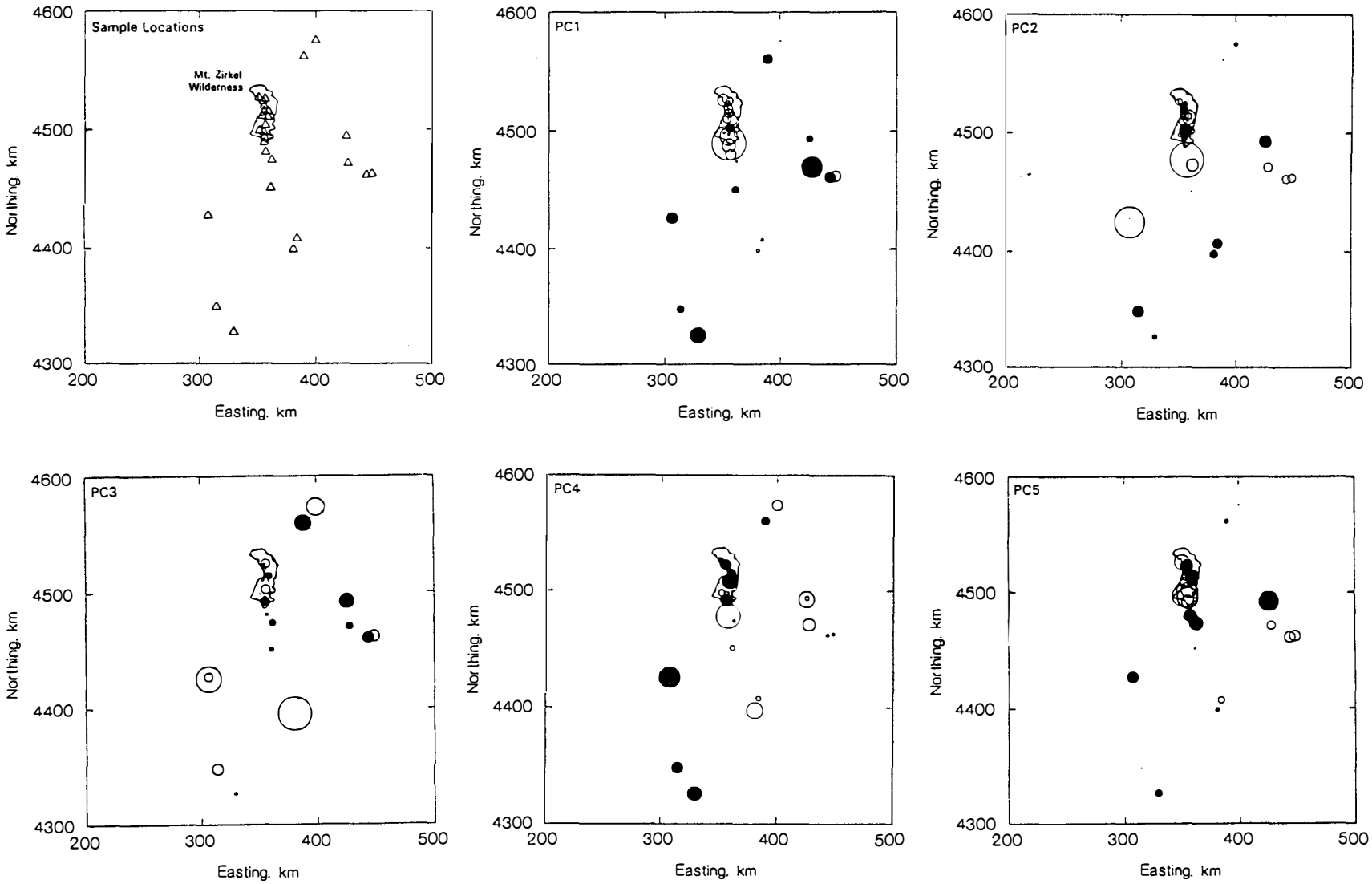

Figure 15. Principal component scores for *Xanthoparmelia* versus location. Circle diameter is proportional to standardized component score (i.e., mean score = 0 and standard deviation = 1, the greater the deviation from the mean the greater the diameter). Open circles have a positive score and filled circles have a negative score.

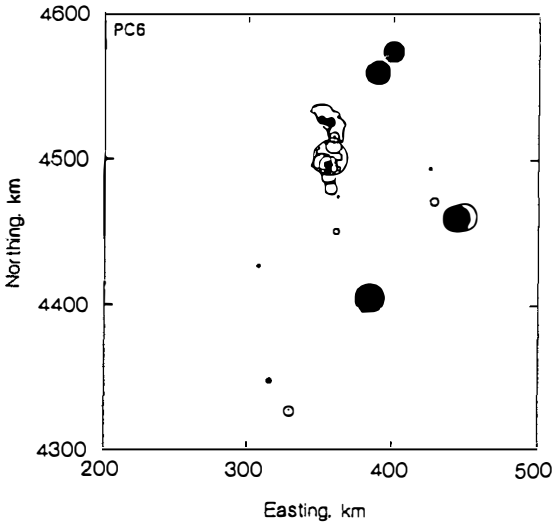

Figure 15. Principal component scores for *Xanthoparmelia* versus location (continued).

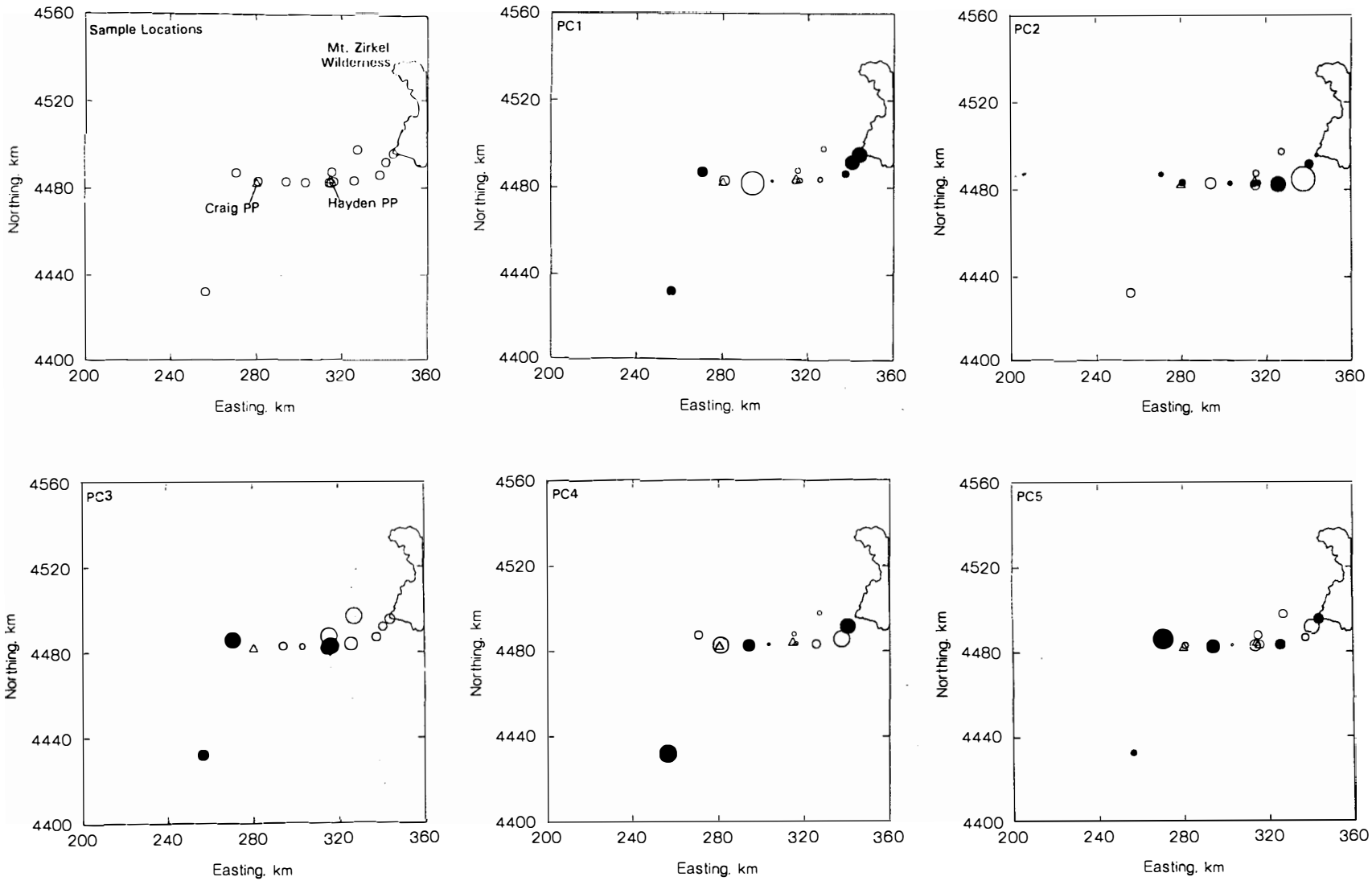

Figure 16. Principal component scores for *Tortula* versus location. Circle diameter is proportional to standardized component score (i.e., mean score = 0 and standard deviation = 1, the greater the deviation from the mean the greater the diameter). Open circles have a positive score and filled circles have a negative score. Power station locations are indicated by △.

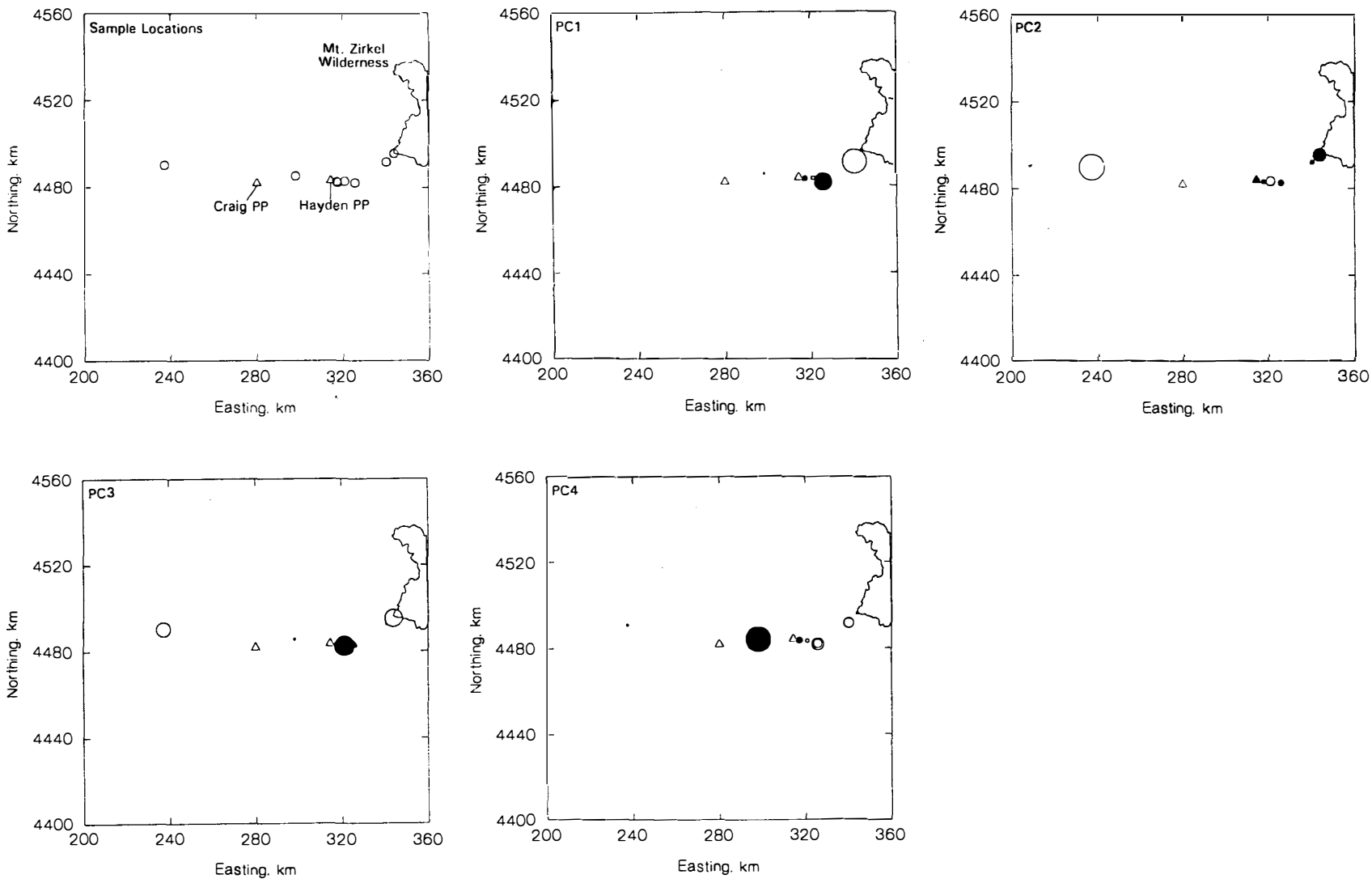

Figure 17. Principal component scores for *Xanthoria* versus location. Circle diameter is proportional to standardized component score (i.e., mean score = 0 and standard deviation = 1, the greater the deviation from the mean the greater the diameter). Open circles have a positive score and filled circles have a negative score. Power station locations are indicated by △.

the vegetation also would likely be indistinguishable from dust contamination. Nevertheless, the PCA models do suggest that there are differences in PC 5 for *Bryoria* (e.g., Mn), in PC I (e.g., Al, Fe, N, S, Si, and Ti) and PC II (e.g., S isotope ratios, B, Ca, and Sr) for *Usnea*, and PC I (e.g., N, K, P, and S) and PC VI (e.g., S isotope ratios) for *Xanthoparmelia* for MZW and Routt National Forest sites compared to other regional sites. The examination of combinations of elements through the PCA may enhance our ability to detect subtle differences among areas compared to single element examinations, but the associations are not always easy to understand.

Spatial Element Trends within MZW and Routt National Forest

Up to this point in our discussion, sites within MZW have been treated as a unit for comparison with regional sites. However, the potential exposure to atmospheric contaminants may vary along the north-south extent of MZW and Routt National Forest. Potentially, sites at the northern extreme of MZW or at the southern extreme of Routt National Forest (e.g., Sarvis Creek Wilderness) may parallel element concentration trends of more distant regional sites much more closely than sites in the southern portion of MZW or in the vicinity of Buffalo and Rabbit Ears Passes. If there were significant spatial trends in element concentrations within this area, it would likely make distinguishing differences between MZW and regional sites more difficult. Thus, we have examined trends within MZW and Routt National Forest by using ANOVA to test the hypothesis that there are no significant differences among north, middle, and south sections of MZW and southern Routt National Forest. MZW was divided in sections of approximately equal north-south extent by sampling team with samples identified as north, middle, and south sections. Sample sites in southern Routt National Forest from Long Lake south to Sarvis Creek Wilderness (SCW) were treated as a fourth section. Even this latter division is somewhat problematic in that the site in SCW on the east side of the Gore Range is likely to have less potential exposure than the sites within the fourth section that are near Rabbit Ears Pass. However, *Bryoria* was not collected at the SCW site and no *Bryoria* or *Usnea* samples were collected in the north section of MZW, hence, only middle and south sections of MZW and the Routt section were compared for the epiphytic lichens. A Tukey HSD post hoc pairwise comparison test was used to examine which specific sections were significantly different from each other.

Only a few elements had a high statistical probability of being different among the sections for each lichen species. Boron, Ca, S, and Zn in *Bryoria* appear to have significant differences among the sections ($p < 0.1$) based on the ANOVA. Boron, S, and S isotope ratios in *Usnea* and Al, B, Be, Li, Na, Ni, Pb, S, S isotope ratios, and Zn in *Xanthoparmelia* appear to have differences in concentrations among the sections. For *Bryoria* and *Usnea* the majority of the concentration differences are attributable to differences between the middle section of MZW and the southern Routt section which suggests that there may be reasonably strong north-south trends in some element concentrations. For *Xanthoparmelia* the most significant differences were largely between the middle and southern sections of MZW.

The sample sites within MZW and Routt National Forest are generally oriented north to south along a reasonably linear traverse. Thus, a plot of element concentration versus

northing provides a fairly representative picture of the north-south distribution of elements within this area. Along this traverse precipitation increases from the north to the south section of MZW and to the Long Lake area of the Routt section and then decreases further to the south towards the SCW. Figures 18-20 show the concentrations for selected element in the lichens and average precipitation along the north-south traverse.

For *Bryoria* and *Usnea* the ANOVA indicated that there were probable concentration differences among the sections for B and S. The concentration plots for both elements generally indicate a concentration maxima in the vicinity of Buffalo Pass to Rabbit Ears Pass--an area of high precipitation in MZW and Routt National Forest. Although the S trend for *Usnea* is less obvious, there is a distinct maximum in the S isotope ratios for *Usnea* in the vicinity of Buffalo Pass. In this same area there are generally minima for Ca, Mg, Mn, and Sr for both epiphytic lichen species, especially compared to more northward in the mid-section of MZW. For *Bryoria* and *Usnea* there are moderate correlations[16] for precipitation and B and inverse correlations for precipitation and Ca, Mn, and Sr (Table 25). Ash concentration for *Usnea* also exhibits some inverse correlation with precipitation. These correlations and distribution patterns suggest that the epiphytic lichens may be acquiring B and S through a mechanism strongly influenced by precipitation or with precipitation as a direct source of the elements. The pattern in S isotope ratios is not obviously mirrored in S concentrations. The inverse patterns in Ca, Mg, Mn, and Sr indicate also that increased precipitation may leach higher concentrations of these elements. Potentially higher acidity precipitation in the Buffalo Pass-Rabbit Ears Pass may promote increased leaching because ion exchange is an important process in uptake of elements by lichens (Richardson, 1995). Higher precipitation may also be more effective at washing the surface of the epiphytic lichens and reducing entrapment of surface dust particles thus accounting for the inverse correlation with ash content and precipitation in *Usnea*.

For *Xanthoparmelia* the ANOVA indicated that numerous elements, Al, B, Be, Li, Na, Ni, Pb, and Zn, and S isotope ratios had moderately significant differences ($p < 0.1$) among the north-south sections. Aluminum, B, and Na had the most significant differences ($p < 0.01$). The Tukey HSD test indicated that generally the middle and south sections of MZW were most different. Among the eight elements and S isotope ratios, B and S isotope ratios were most highly correlated with precipitation. In the principal component analysis Al, Be, Li, and Ni were associated and may be related due to soil or rock contributions to the lichen. Boron also was associated to these elements to some extent and the north-south patterns for Al, B, and Be are quite similar (Figure 20). The relationship between precipitation and concentration of these elements in *Xanthoparmelia* may be due to atmospheric washout of the particles and subsequent uptake and/or adsorption of the elements on to the surfaces of the lichen during snow melt--a process that is much less likely to influence the concentration of elements in the epiphytic lichens to the same extent. The inverse relationship of precipitation and Ca, Mg, Mn, and Sr concentrations observed in the epiphytic lichens was not obvious for the *Xanthoparmelia*.

[16]Correlation coefficients (r) are for the nonparametric Spearman's rank correlation.

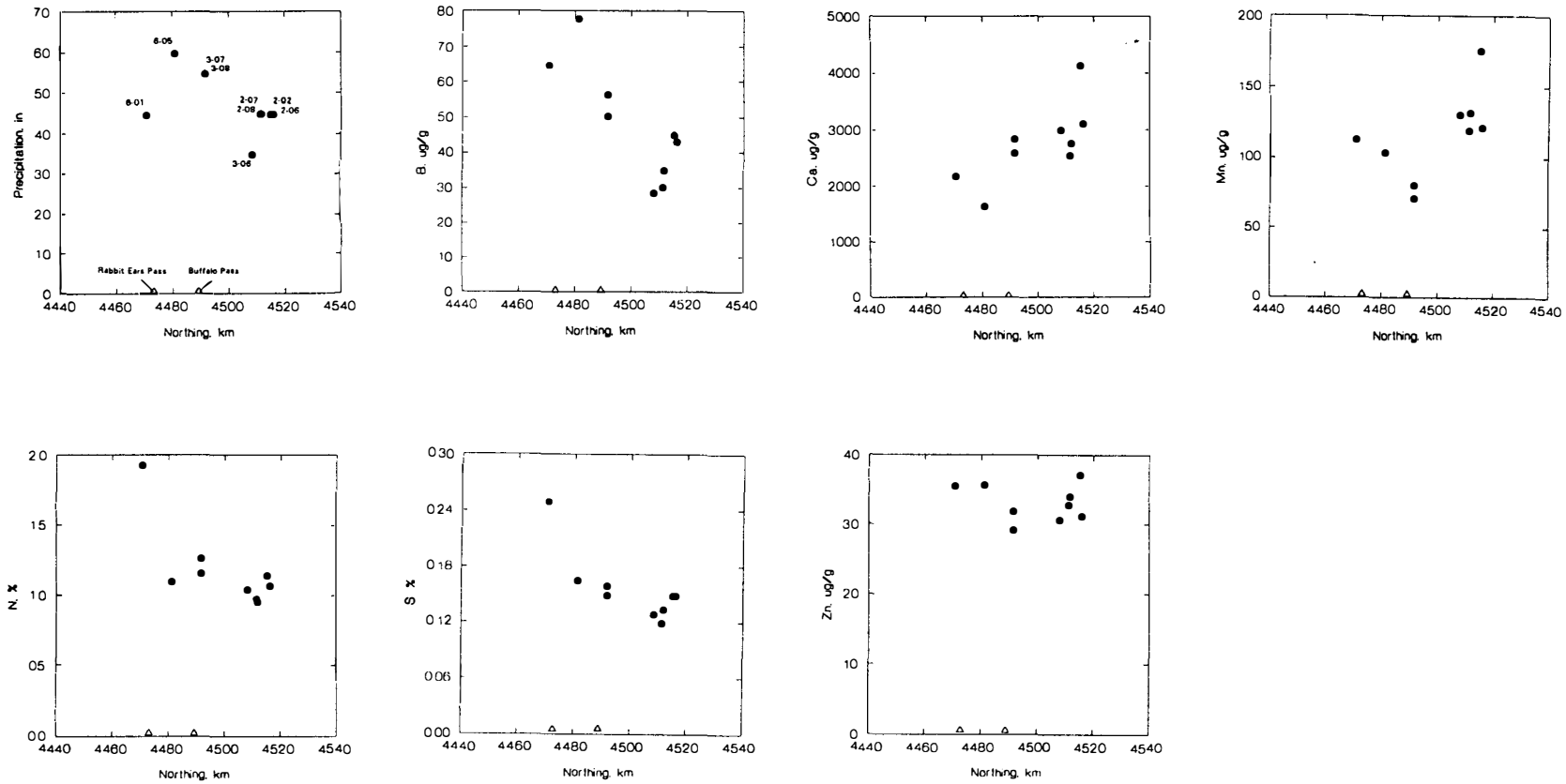

Figure 18. Concentration of selected elements in *Bryoria* versus Northing along the north-south trending traverse in MZW and Routt National Forest. Approximate locations for Buffalo and Rabbit Ears Passes are indicated along the Northing-axis by △.

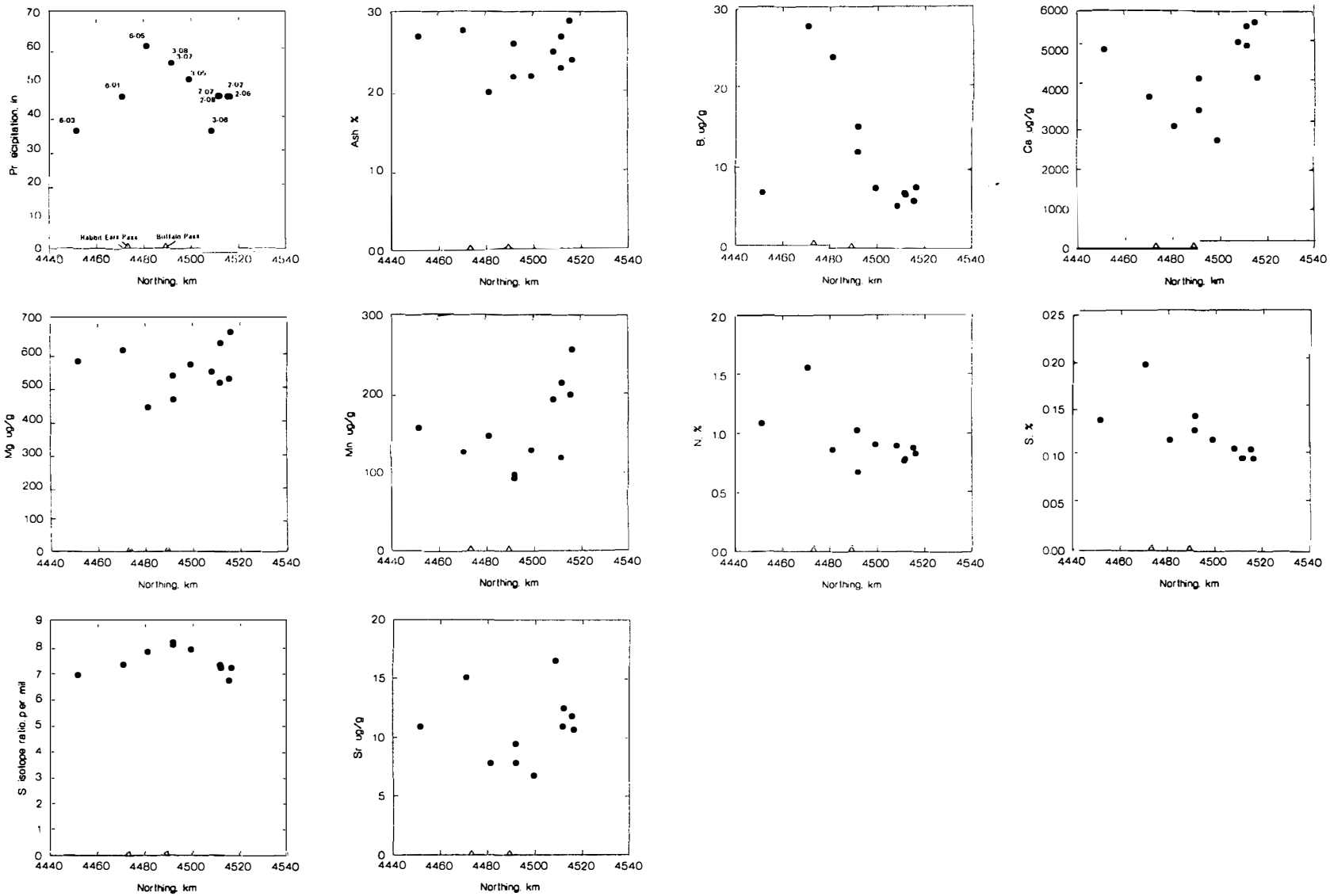

Figure 19. Concentration of selected elements in *Usnea* versus Northing along the north-south trending traverse in MZW and Routt National Forest. Approximate locations for Buffalo and Rabbit Ears Passes are indicated along the Northing-axis by △.

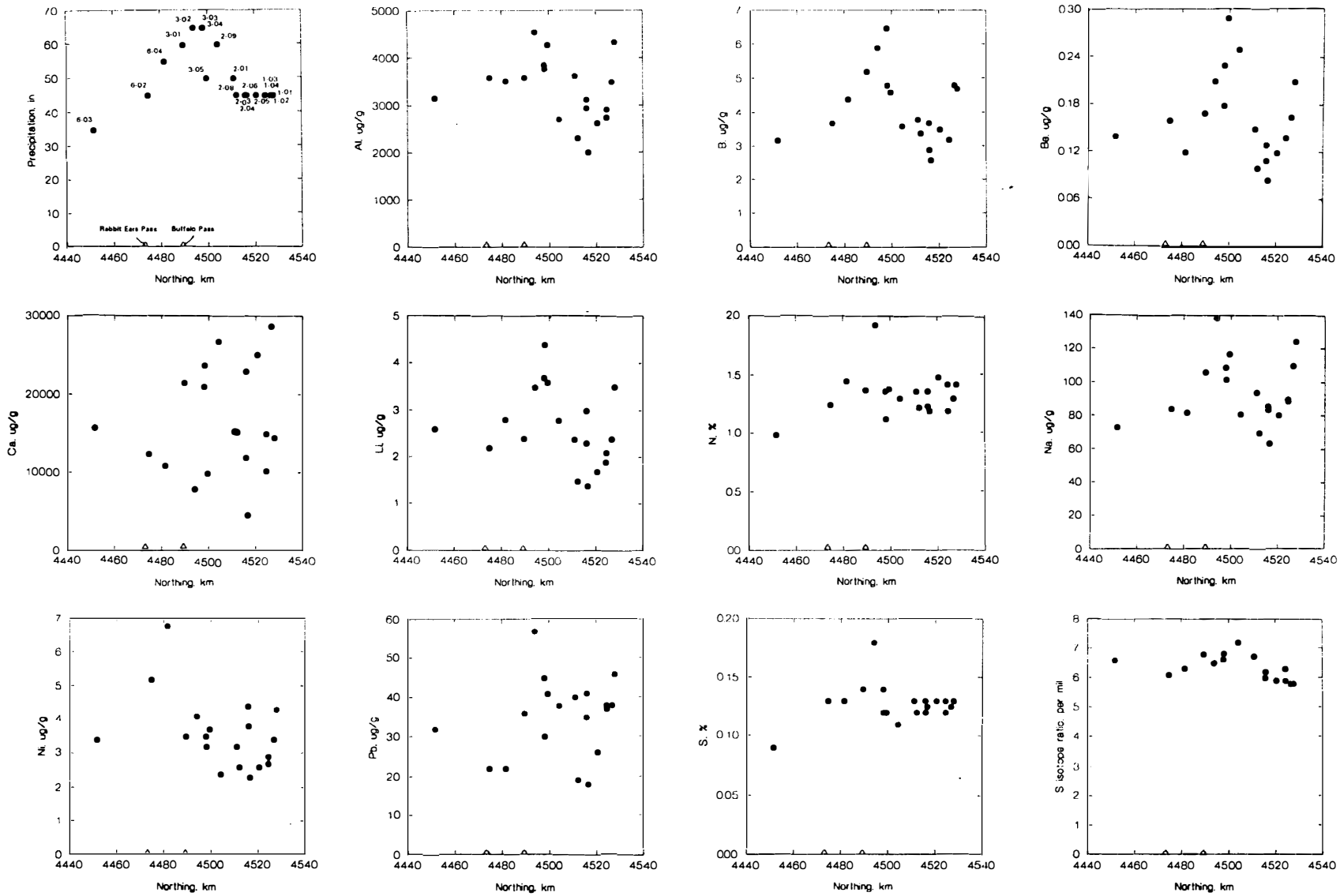

Figure 20. Concentration of selected elements in *Xanthoparmelia* versus Northing along the north-south trending traverse in MZW and Routt National Forest. Approximate locations for Buffalo and Rabbit Ears Passes are indicated along the Northing-axis by △.

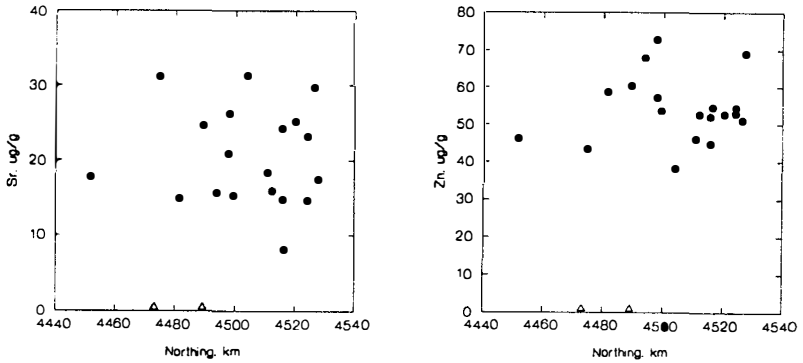

Figure 20. Concentration of selected elements in *Xanthoparmelia* versus Northing along the north-south trending traverse in MZW and Routt National Forest (continued).

Table 25. Spearman rank correlation coefficients for precipitation and selected elements for sites in MZW and Routt National Forest.

	Correlation coefficient with average precipitation		
Element	*Bryoria* (n = 9)	*Usnea* (n = 11)	*Xanthoparmelia* (n = 19)
Al	0.44	0.19	0.53*
Ash	-0.03	-0.58	0.42
B	0.78**	0.66*	0.72**
Ba			
Be	--	--	0.60**
Ca	-0.48	-0.71*	0.07
Cd			
Cr			
Cu	0.30	-0.21	0.48*
Fe			
K			
Li	--	--	0.61**
Mg	0.07	-0.54	0.40
Mn	-0.74*	-0.52	0.15
N	0.43	-0.25	0.33
Na	0.21	-0.02	0.47*
Ni			
P			
Pb			
S	0.54	0.26	0.37
$\delta^{34}S$	--	0.82**	0.64**
Si			
Sr	-0.80**	-0.78**	0.16
Ti			
Zn	0.12	0.30	0.46*

* Significant $p < 0.05$
** Significant $p < 0.01$

For most elements in the three lichens there do not appear to be strong north-south trends that would influence our ability to distinguish differences among the MZW sites compared to the regional sites. However, for elements such as B and S and for S isotope ratios, sites in the high precipitation areas near Buffalo Pass-Rabbit Ears Pass may be more significantly different from more distant regional sites than our previous MZW or distance grouped analyzes would indicate. These are also the sites that are closest to the power stations and directly downwind.

Spatial Element Trends within the Yampa Valley

As noted above, distinct spatial trends within the valley for most component scores (Figure 17) are not readily obvious. However, if we apply linear regression analysis to PCA scores with distance from the Craig Power Station as the independent variable for those samples of *Tortula* that were collected in the immediate vicinity of or to the east of the station (n = 12), we do see a significant decrease in PC I scores with distance from the station (Figure 16). The coefficient of determination ($r^2 = 0.66$) indicates that 66% of the variation in PC I scores is accounted for by variation in the distance from the power station and the slope of the regression line is significantly different from zero ($p < 0.01$). The coefficient of determination increases to 0.87 when the regression is applied only to the six samples that are east of the Hayden station along a reasonably linear traverse to the WNW. Samples to the west of the Craig Power Station have PC I scores that are most similar to scores for the eastern most *Tortula* samples. As seen in Table 23, PC I scores for *Tortula* are predominantly controlled by ash, Al, Be, Cr, Fe, Li, Mg, and Na concentrations. Coefficients of determination for the linear regression of the concentration of these elements versus distance east of the two power stations are given in Table 26. Element concentrations versus Easting are shown in Figure 21. Distance from the Craig station accounts for a large proportion of the variation in the ash, Al, Be, and Na concentrations. The concentration of these lithophilic elements in samples to the west of the Craig Power Station are generally small compared to concentrations in the vicinity of the station and most similar to the eastern most samples.

Coefficients of determination are shown also in Table 26 for a linear regression for *Tortula* element concentrations at six sites versus distance east of the Hayden station. Although r^2 increased dramatically for some elements (e.g., N and S), it is not obvious what these inverse distance trends truly mean (due to scatter in the data when looking at all points; and sites west of Craig have some of the highest concentrations). However, in some cases the inverse distance relationship is stronger (e.g., B) and the western-most sites are low in concentration compared to sites near the power stations.

Stable S isotope ratios in *Tortula* appear to indicate that there are two sample populations with distinctly different isotopic signatures (Figure 22). Eight out of twelve samples had isotopic ratios ranging from about +4.4 to +6.8‰, whereas the remaining one third of the samples ranged from about +0.6 to +2.3‰. The latter samples are distributed throughout the east-west traverse. It is possible that these lighter isotopic values are due to gypsiferous or various shale derived soils (Williams and Clark, 1994) within the valley that may have a characteristically lighter isotopic signature.

Table 26. Coefficients of determination for linear regression of principal components and selected elements versus distance east of the power stations.

	Tortula		*Xanthoria*
	East of Craig[1] (n = 12)	East of Hayden[2] (n = 6)	East of Hayden (n=7)
PC I	0.66*	0.87*	0.31
PC II	< 0.01	< 0.01	0.37
PC III	0.08	0.65*	0.55
PC IV	0.01	0.06	0.05
PC V	< 0.01	0.02	--
Al	0.81*	0.79*	0.25
Ash	0.68*	0.71*	0.17
B	0.47*	0.68*	0.84*
Be	0.72*	0.64	0.08
Ca	< 0.01	0.02	0.70*
Cr	0.52*	0.69*	0.19
Cu	0.40	0.47	0.61*
Fe	0.54*	0.55	0.23
Li	0.50*	0.83*	0.14
Mg	0.61*	0.77*	0.42
N	< 0.01	0.26	0.22
Na	0.71*	0.98*	0.10
Ti	0.05	0.60	0.08
Zn	0.05	0.10	0.60*

[1]Sites with Easting > 280 km.
[2]Sites with bearing > 50° and < 160°.
*Slope of the regression line is significantly different from zero ($p < 0.05$).

Seven out of nine sites where *Xanthoria* was collected were located to the east of the Hayden Power Station along a reasonably linear traverse bearing from the station to the WNW. Regression analysis of the PCA scores is not very helpful in understanding trends within the Yampa Valley, although PC II scores clearly decrease from west to east within the valley (Figure 17) and PC III and IV scores tend to increase to the east of Hayden. However, in examining the individual elements only two elements B and Zn have strong trends to the east of the Hayden Power Station. Boron is inversely related to distance east of the station and the western-most site is low in concentration compared to the sites near the power station whereas Zn increases with distance and the western-most site is intermediate in concentration

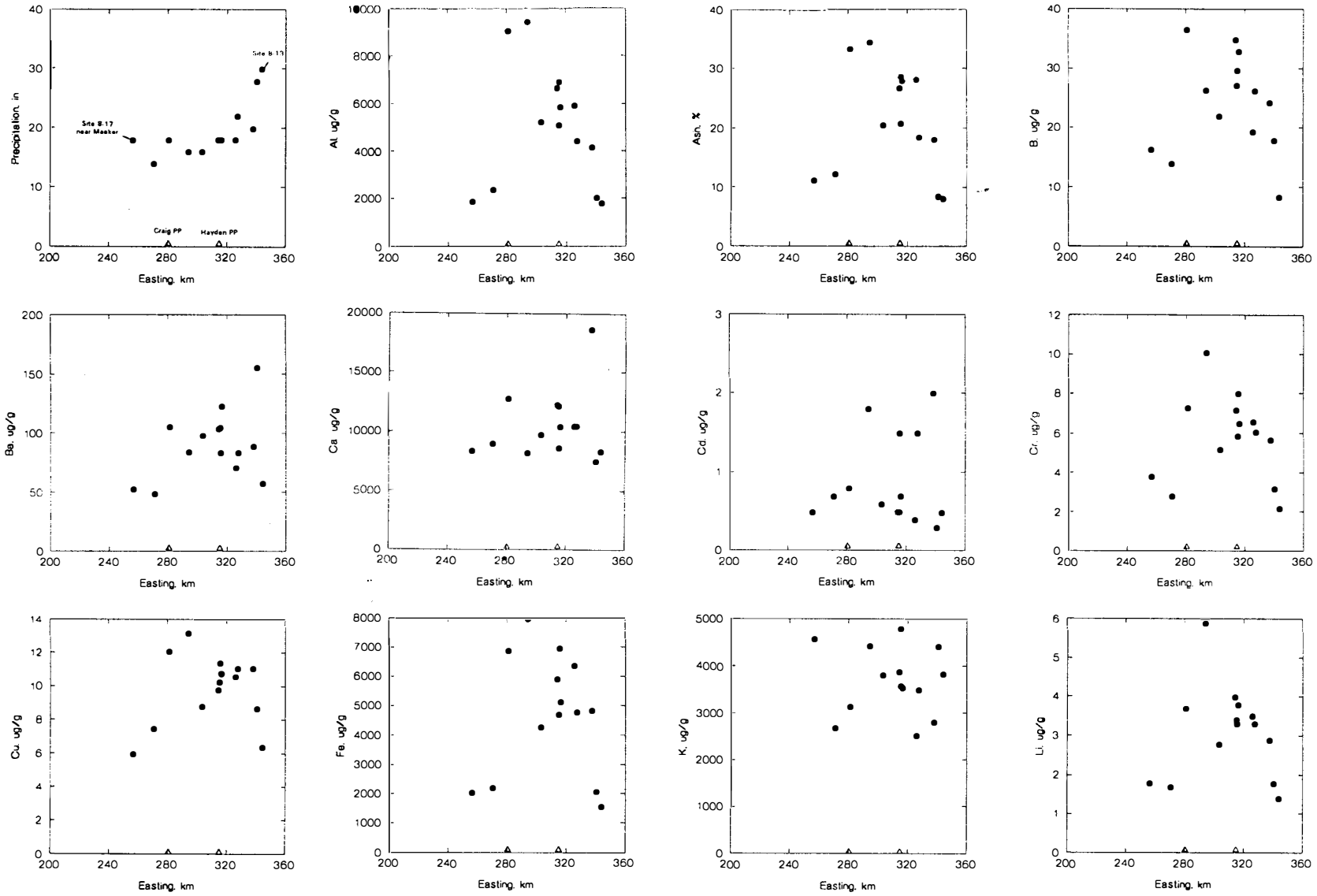

Figure 21. Concentration of elements in *Tortula* versus Easting in the Yampa Valley. Power station locations are indicated along the Easting-axis by △.

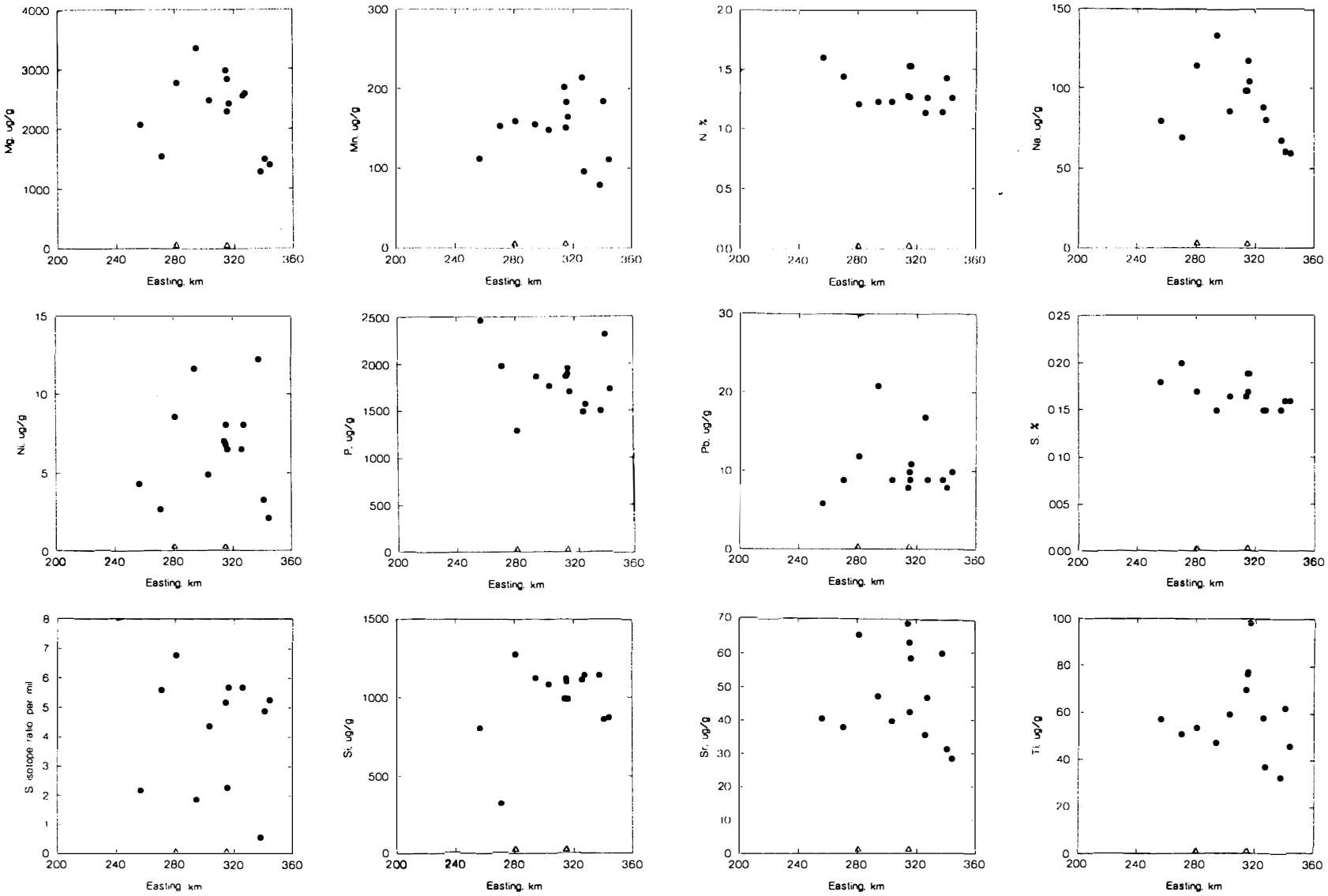

Figure 21. Concentration of elements in *Tortula* versus Easting in the Yampa Valley (continued).

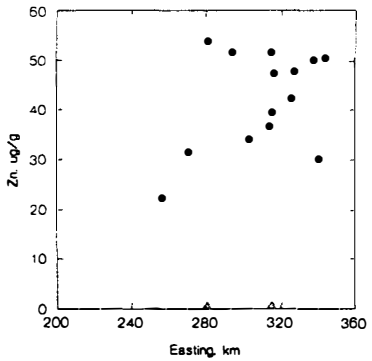

Figure 21. Concentration of elements in *Tortula* versus Easting in the Yampa Valley (continued).

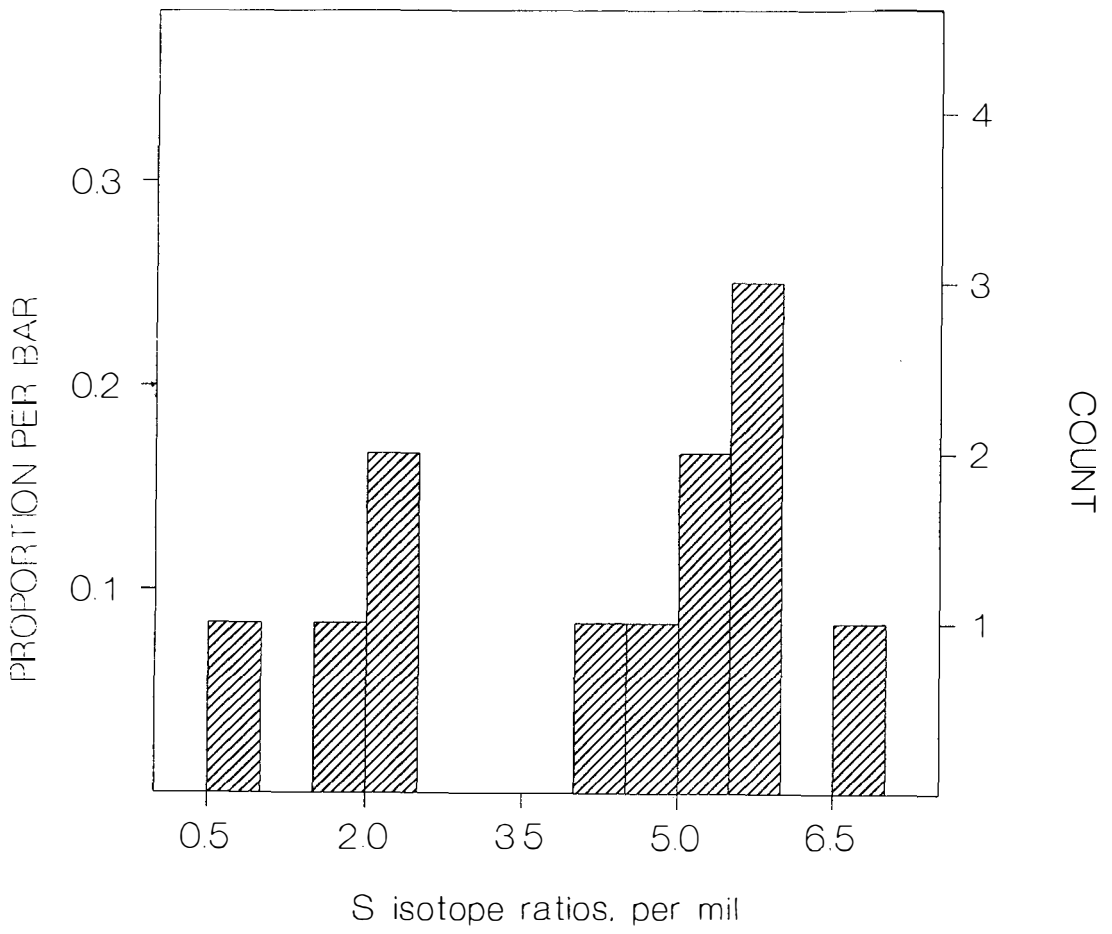

Figure 22. Histogram of stable S isotope ratios in *Tortula* in the Yampa Valley.

compared to the other sites (Figure 23). For the other elements there is a large amount of variability in the data and spatial trends are not obvious.

For the moss and the lichen species there are consistent decreasing B concentration trends to the east of the power stations. Other lithophilic elements such as Al, Fe, and Na also decrease in concentration in an eastward direction for the moss. Dry deposition of fly ash may be strongly influencing these trends, but distinguishing between fly ash and soil or eolian dust contamination is difficult. Elevation and precipitation increase in an eastward direction (Figures 21 and 23). Although an increase in precipitation may introduce additional elements, it may also provide for more effective washing of the moss or lichen surface and decrease the uptake or entrapment of elements from fly ash or dust. Spatial variability in the geochemistry of the local soils has not been measured and how this might affect the moss and lichen chemistry is not known.

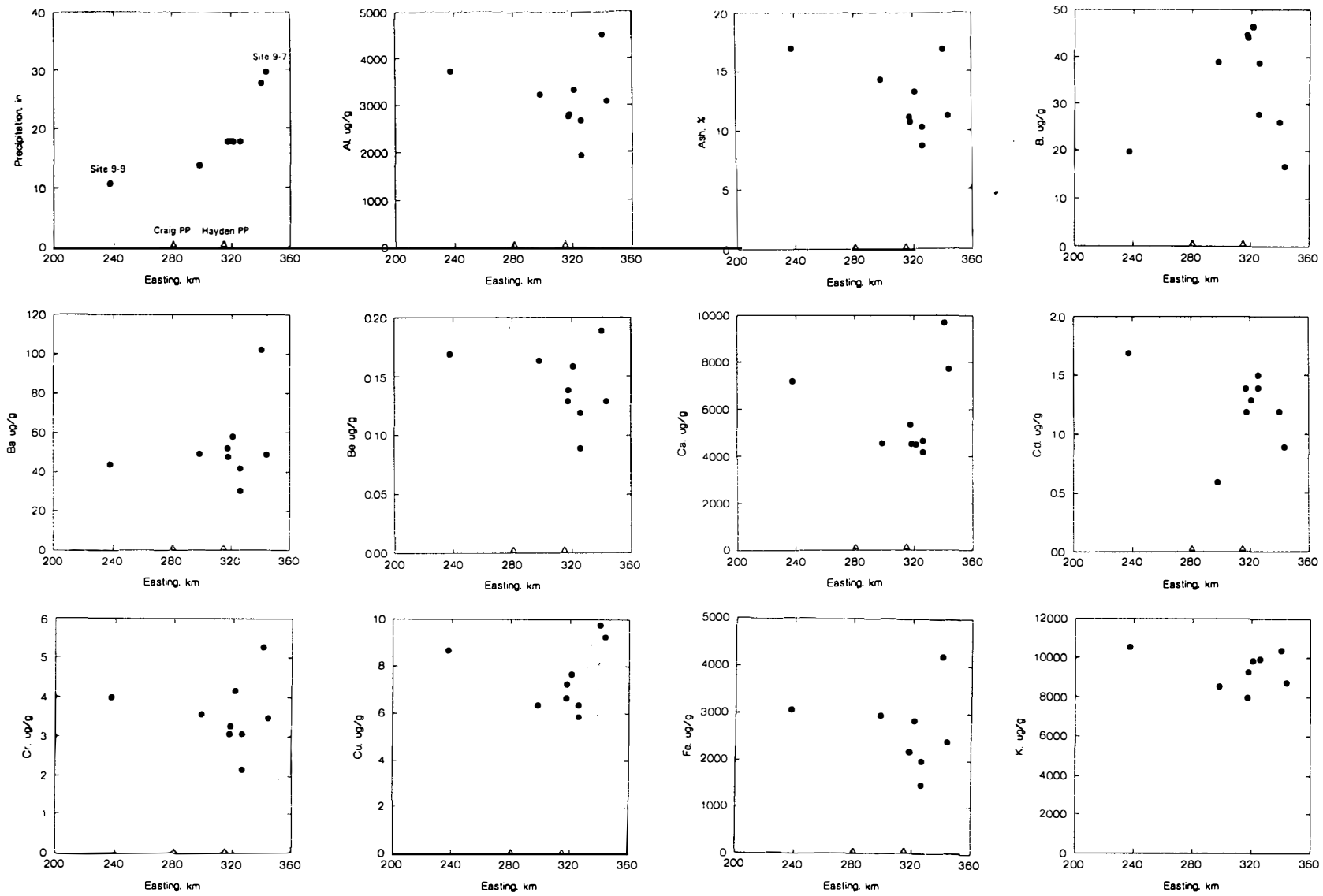

Figure 23. Concentration of elements in *Xanthoria* versus Easting in the Yampa Valley. Power station locations are indicated along the Easting-axis by △.

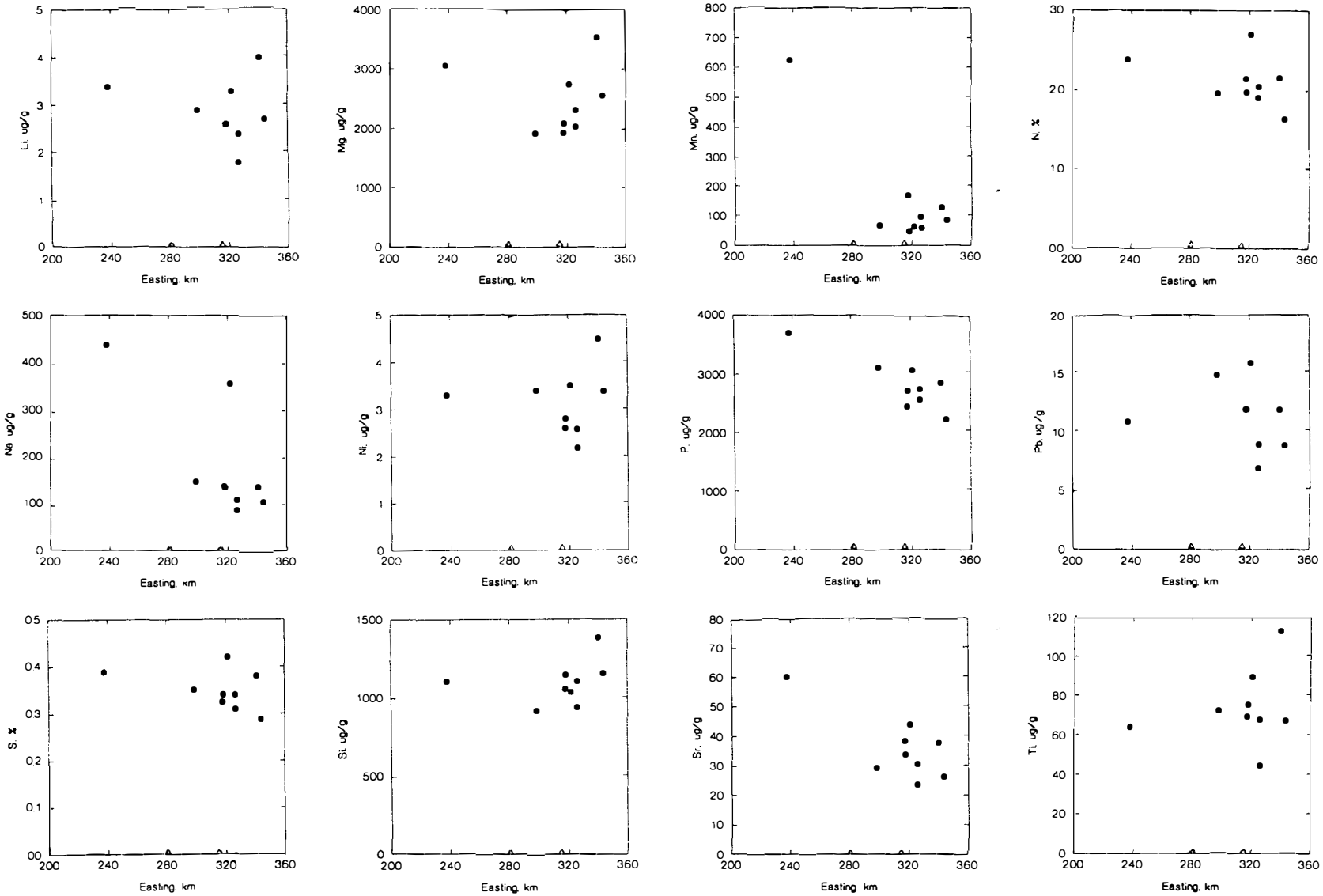

Figure 23. Concentration of elements in *Xanthoria* versus Easting in the Yampa Valley (continued).

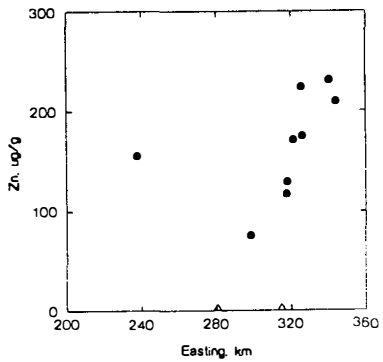

Figure 23. Concentration of elements in *Xanthoria* versus Easting in the Yampa Valley (continued).

Lead and Sulfur Isotopic Signatures

Lead isotopic ratios were determined in a small proportion of the vegetation samples (6 *Tortula* samples and 11 *Xanthoparmelia* samples) and two coal samples in order to test the feasibility of using lead isotope ratios in these samples as tracers of lead from power station emissions. The two whole coal samples included a composite sample of the Q seam from the Trapper Mine and a composite sample from the Wadge seam in the Seneca 2 Mine. It is unclear how representative these samples are of the coal being consumed at the power stations or how representative the whole coal Pb isotopic signature is of the Pb in the power station emissions. However, we assume that there is relatively little fractionation of the Pb isotopes during combustion and that the Pb isotopic signatures of sample coals are within the range of values currently being emitted.

Among the limited samples analyzed there appears to be no relationship between Pb concentration and Pb isotope ratios (Figure 24). This is not unexpected based on the lack of correlation of Pb content in the lichens and moss with respect to distance from the power stations. Various sources can contribute Pb to the vegetation, eolian dust, local soils, and rock substrate, as well as potentially coal combustion emissions. The coals from the two mines have similar $^{208}Pb/^{204}Pb$ ratios and somewhat different $^{206}Pb/^{204}Pb$ ratios (replication error $< \pm 0.1$). Generally, as seen in Figures 24 and 25, the Pb isotopic signatures of the vegetation do not match the signature of the coals, except for the data from the two moss samples near the Craig Power Station. The Pb isotope ratios for the limited test of air particulates (Aleinikoff and Peterman, unpublished data from a feasibility study of air filters collected by the Colorado State Health Department in November 1993 and January 1994) from near MZW also do not resemble the coals or most of the lichens and mosses. The moss samples collected in the Yampa Valley tend to have more radiogenic Pb isotope signatures than the lichens collected in the mountainous areas. This is also true for the moss and lichen samples collected at the same location (8-15) at the western edge of MZW. These results suggest that the Pb isotope signatures of the Pb sources for the two species are moderately different and/or reflect different uptake mechanisms. In another study this type of difference was attributed to radiogenic Pb uptake from soil solution (Carignan and Gariepy, 1995). Fossil fuels usually have radiogenic isotope signatures (Chow and Earl, 1972; Hurst and others, 1993), but with the limited data available there is no clear indication that combustion emissions are significantly contributing Pb to the vegetation sampled, although the Hayden station apparently emits about 180 kg yr^{-1} and the Craig station about 30 kg yr^{-1} (Colorado State Health Department, written communication). Because the Pb isotope ratios in the moss samples near the power stations are distinctly larger and more radiogenic than the coal samples analyzed, it is possible that the whole coal sample Pb isotopic signatures are truly not representative of Pb emissions as we have assumed. It appears that more analyses of potential Pb sources are required before Pb isotopic signatures could be used as a viable tool for assessing the dispersion patterns of coal combustion emissions in this area.

Stable S isotope ratios of coal, moss (*Tortula*), and two lichen species (*Usnea* and *Xanthoparmelia*) were determined as a potential tracer of the dispersion of coal combustion emissions. Stable S isotope ratios were determined in one composite coal sample from the Trapper Mine Q seam and four composite samples from the Seneca 2 Mine Wadge seam. In

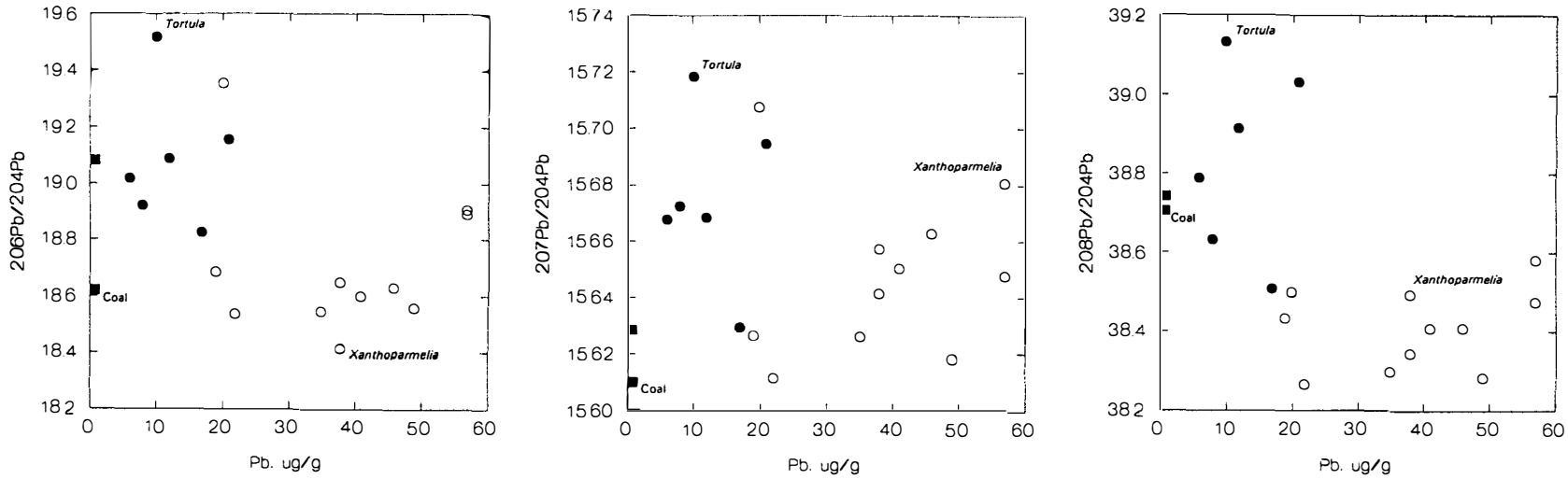

Figure 24. Lead isotope ratios in *Xanthoparmelia*, *Tortula*, and coal versus lead concentration (lead concentration in coal arbitrarily set at zero).

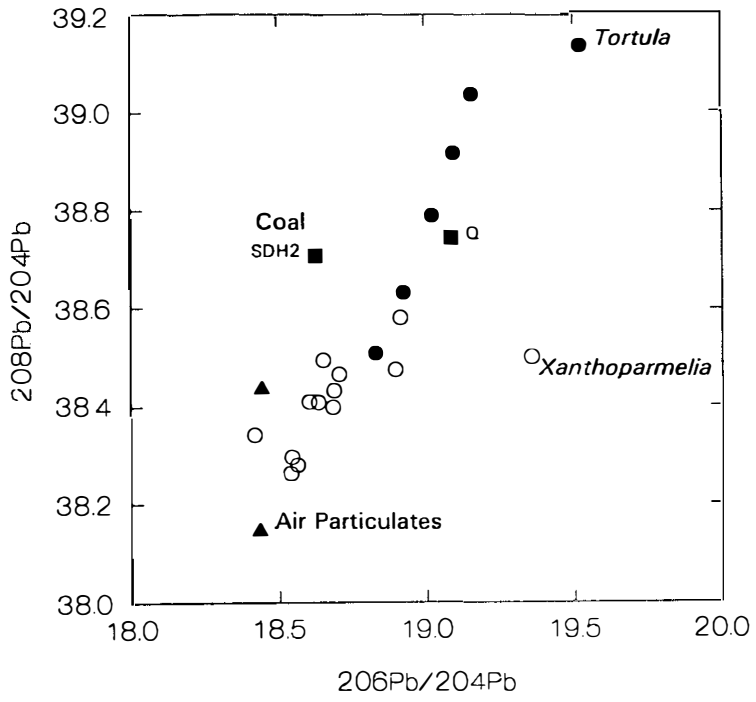

Figure 25. Lead isotope ratios in *Xanthoparmelia*, *Tortula*, coal, and air particulates (Peterman and Aleinikoff, unpublished data from pilot study).

the S isotope determination the whole coal was combusted in a high pressure oxygen atmosphere. This procedure effectively oxidizes all organic S and potentially a large proportion of the reduced inorganic forms of S present (e.g., disseminated pyrite). Thus, although the procedure preferentially determines the isotopic signature of organic forms of S, for coals such as from the Yampa Valley Wadge and Q seams that are very low in inorganic forms of S this procedure provides a reasonable determination of the whole coal isotopic signature. Others have determined specifically the isotopic signature of organic S and pyritic S in Yampa Valley coals (Hackley and Anderson, 1986; Holmes and Brownfield, 1992). Hackley and Anderson found that in the low sulfur (total S = 0.45%) Wadge coal, from an undisclosed mine in northwestern Colorado, 85-95% of total S was in organic S forms with $\delta^{34}S$ with an average value of +6.6 ± 1.4‰ (range = +4.3 to +8.1‰). Massive pyrite had very negative isotopic signatures (-43.3 to -52.0‰). Disseminated pyrite was in too low abundance to measure isotopically. Organic sulfur in coal from the Green River coal region of southwestern Wyoming and the Hanna Basin in south-central Wyoming had average stable S isotope ratios of +5.2 ± 2.3‰ and +6.9 ± 4.2‰, respectively (Hackley and Anderson, 1986). For the coal seams sampled in the three areas, the stable S isotope ratios for the

organic sulfur are not greatly different, although there was much greater variability in the isotope ratios at the Wyoming sites compared to the northwestern Colorado site.

At two northwestern Colorado mines, Holmes and Brownfield (1992) found heavier (i.e., more positive) S isotopic ratios for Wadge seam organic S than Hackley and Anderson (1986) measured in the same coal basin. At the Edna Mine, the $\delta^{34}S$ for organic S in the Wadge seam averaged +8.8 ± 2.2‰ (range = +5.3 to +13.5‰). Partings within the Wadge seam had $\delta^{34}S$ values of -4.4 to -11.8‰. The overlaying Lennox seam coal had much heavier organic S isotope ratios (average $\delta^{34}S$ = +15.8 ± 2.9‰) presumably due to a strong marine influence during or after peat deposition. In the Yampa Mine, the Wadge seam organic S $\delta^{34}S$ averaged +8.9 ± 0.8‰ and the Lennox seam averaged +17.6 ± 1.4‰. We measured nominally whole coal Wadge seam $\delta^{34}S$ values that averaged +9.9 ± 0.5‰ within four drill cores from the Seneca 2 Mine and a Q seam $\delta^{34}S$ value of +5.4‰ for the Trapper Mine (Figure 26). Based on the single lighter $\delta^{34}S$ isotopic measurement for the Q bed, this low sulfur coal appears to have had less marine influence than the low sulfur Seneca 2 Mine Wadge seam from the eastern portion of the Yampa Valley.

Total S emissions from the two power stations should have an isotopic signature that represents a proportionate mixture of the two coal sources falling within the range of +5 to +10‰. Blending of the Lennox coal with the Wadge coal at the Hayden Power Station would cause the S isotopic ratio of emissions to be even heavier. We speculate that the Wolf Creek seam has a lighter S isotopic signature than the Wadge seam because of its lower position in the stratigraphic sequence and probable decreased marine influence. Thus, a mixture of the Wadge and Wolf Creek seam is likely to have an isotopic signature that is intermediate in the +5 to +10‰ range. Inclusion of partings with higher pyrite concentrations and lighter isotopic ratios would cause more negative isotopic signatures. The blending of coals from several seams and mines and the inherent heterogeneity of the coals will contribute to some variability over time of the S isotope ratio of power station emissions. However, because of the proximity of the power stations to MZW and the nature of the coals burned, we suspect that the time-averaged atmospheric S isotope signature, if it were measured directly, would fall at the heavier (more positive) end of the range, particularly for the Hayden station.

Newman and others (1975) found that flue gas SO_2 from a coal-fired power plant had an S isotopic value that varied by more than 2‰ over time, but was representative of the coal combusted when the coal was from a uniform source. In this study, SO_3 formation during combustion represented about 1% of the SO_2 emissions and in an earlier study was found to be slightly enriched in ^{34}S by 1.5‰ compared to the SO_2 (Forest and others, 1973; Krouse and Grinenko, 1991). They hypothesized that there should be a large difference in $\delta^{34}S$ for SO_4^{2-} formed via oxidation and the original SO_2. However, in several power plant studies they did not observe the anticipated shift of +20‰ and attributed the lack of shift to little oxidation (<5%) of SO_2 to SO_4^{2-} potentially influenced by low particle loadings (Forrest and Newman, 1977). They also observed that most of the plume drop out of sulfate occurred within a few kilometers of the power plant. In a more widespread study of fossil fuel related S emissions in the northeast U.S. conducted by the same research group (Krouse and Grinenko, 1991), atmospheric sulfate averaged more positive $\delta^{34}S$ values by about 2.6‰ than SO_2. Little work has been done on the isotopic signature of S in fly ash, but in a

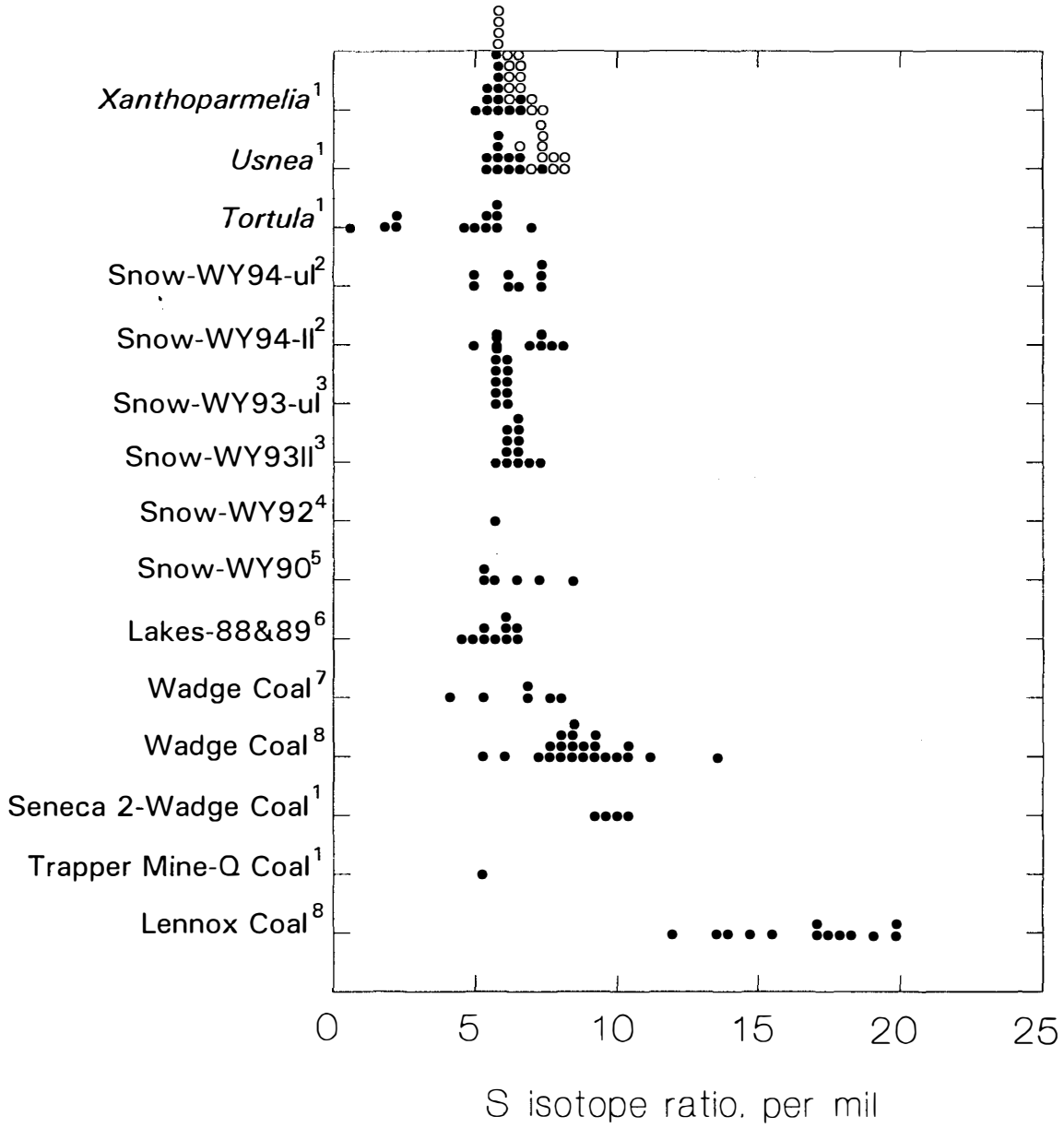

Figure 26. Distribution of stable S isotope ratios in vegetation, snow, lake water, and coal. Notes: [1]This study; for the lichens, the MZW and RNF samples are indicated as open circles and all other regional samples as filled circles. [2]Ingersoll, 1995; snow from vicinity of MZW, RNF, and FTW water year 1994, ul=upper layer (approx. Jan-April, 1994) and ll=lower layer (approx. Sept-Dec, 1993). [3]Turk, unpublished data; snow from MZW and RNF sites water year 1993, ul=approx. Jan-April 1993 and ll=approx. Sept-Dec 1992. [4]Finley and others, 1995; snow from MBNF water year 1992. [5]Turk and others, 1993; snow from MZW, RNF, RMNP, and MBNF water year 1990. [6]Turk and others, 1993; lake water from MZW and RNF 1988 and 1989. [7]Hackley and Anderson, 1986; Wadge coal organic S. [8]Holmes and Brownfield, 1992; Wadge and Lennox coal organic S.

Russian study, fly ash had an isotopic ratio that was intermediate between the ratios of two coals blended for combustion (Krouse and Grinenko, 1991). Regardless of whether oxidation occurs during combustion or in some atmospheric process, the S isotopic signature of emissions should be equal to or potentially more positive than the original coal combusted.

Alpine lakes with low acid neutralizing capacity in MZW and snow have been used to help understand atmospheric sulfate deposition in northwest Colorado (Ingersoll, 1995; Turk and others, 1992; Turk and others, 1993; Turk, unpublished data). Stable S isotope ratios of snow have been a key to understanding sulfate deposition in the region. For example, during 1988-1990 snow had isotopic ratios of +7.3 to +8.4‰ at Rabbit Ears Pass downwind of the Yampa Valley power stations, whereas snow in Medicine Bow National Forest (MBNF) in Wyoming and Flat Tops Wilderness had ratios of +5.4‰ (Turk and others, 1993). Mt. Evans' snow averaged +4.0‰ and in Rocky Mountain National Park it was +6.6‰. Lakes near Buffalo Pass and just north of Rabbit Ears Pass had isotopic values ranging from +5.7 to +6.7‰. Lakes in MZW north of the Buffalo Pass area, Lake Elbert and Seven Lakes, ranged from +4.4 to +5.4‰ (Figure 26). Finley and others (1995) estimated the atmospherically derived sulfate at Glacier Lakes in MBNF had a $\delta^{34}S$ value of +5.6‰ based upon snow measurements in the same period. In 1992, snow in MZW and the vicinity downwind of the Yampa Valley power stations had S isotope ratios of +7 to +9‰, whereas sites upwind or at much greater distance from the power stations ranged from +4 to +6 (Turk and others, 1992). In the first half of 1993, the Hayden Power Station partially shutdown significantly reducing its emissions for SO_2. Snow in the MZW and Rabbit Ears Pass area of Routt National Forest had isotopically heavy $\delta^{34}S$ values (+4.6 to +7.5‰) for the 1993 snow year, but values that were somewhat lighter than in 1992 for the same sites (Turk, unpublished data) (Figure 26).

In the 1994 water year, the snowfall period just prior to our sampling of lichens, S isotope ratios were determined in snow from sites in Routt National Forest and White River National Forest (Ingersoll, 1995) (Figure 26). Sites generally upwind of the power stations on or near the Flat Tops plateau had S isotope ratios that ranged from +4.9 to +6.1‰ with an average of +5.4 ± 0.5‰ for upper and lower strata of snow. Upper and lower strata of snow samples from Buffalo and Rabbit Ears Passes ranged from +6.7 to +7.7 with an average of +7.3 ± 0.3‰, whereas samples from Dry Lake and Elk River in Routt National Forest ranged from +6.3 to +8.0‰. The snow and lake isotopic signatures suggest a local isotopically heavy source of atmospheric S such as would potentially result from a mixing within the airshed of S emissions from the two power stations.

Stable S isotope ratios were determined in snow at numerous other sites along the Continental Divide during the 1994 water year (Turk and Ingersoll, USGS, unpublished data). Snowpack in Colorado from Berthoud Pass southward along the Continental Divide to Wolf Creek Pass had S isotope ratios that ranged from +4.0 to +5.9‰. In south-central Wyoming, S isotope ratios in snow were +6.6‰ at Divide Peak, +7.2 at Old Battle Mountain, and +7.5‰ at South Pass. At sites in northwestern Wyoming, S isotope ratios ranged from +5.2 to +8‰ with most ratios lighter (i.e., more negative) than +7‰. The heavy isotopic signatures in snow in MZW and Routt National Forest (i.e., > +7‰) clearly represent a maximum for northwest Colorado and within the state as a whole. Although some similar heavy isotope ratios have been observed in the same water year in west-central and

northwestern Wyoming along the Continental Divide, we do not believe that these ratios indicate the same S source for the entire northwest Colorado and western Wyoming region.

We have previously discussed some of the trends of S isotope ratios in the lichens and moss collected in this study. Stable S isotope ratios for *Usnea* averaged +7.2‰ for all sites within 60 km of the Hayden Power Station and +6.0‰ for the sites that were greater than 100 km from the station. The heavier isotopic signature for the close in and largely downwind sites was statistically different ($p < 0.05$, two sample t test) from the other regional sites. The isotopic signature for *Xanthoparmelia* at the <60 km sites (+6.3‰) was only weakly different ($p = 0.15$) from the more distant sites (+5.7‰). The difference between regions was smaller for the *Xanthoparmelia* (0.6‰) compared to the *Usnea* difference (1.2‰). The *Xanthoparmelia* also had lower isotopic ratios than the *Usnea* within MZW and the vicinity. *Usnea* was not collected at as many sites and not always the same sites as *Xanthoparmelia* and this may account for some of the difference in average values, but we suspect that a portion of the difference may be due to differences in S sources or uptake mechanisms. *Usnea* may be more impacted by SO_2 compared to SO_4^{2-} in particulates versus the rock-growing *Xanthoparmelia* and substrate probably influences the *Xanthoparmelia* more than the *Usnea*. Fractionation of S isotopes during throughfall is suspected to be small. No significant difference was found in S isotope ratios for precipitation versus throughfall in a northern hardwood forest (Stam and others, 1992). Canopy exposure differences may influence the S isotopic ratios somewhat, but because snow is a major source of sulfate in this area of high winds and powder snow (Peters and Leavesley, 1995; Turk and others, 1992) and dryfall is a minor source of sulfate deposition at high elevations in the Rocky Mountains (Turk and Spahr, 1989), these differences are also expected to be negligible.

Usnea and *Xanthoparmelia* were collected at 11 locations that were at the same site or at sites within 1 km of each other. In 9 of 11 cases the S isotopic ratio for *Usnea* was greater than for *Xanthoparmelia*. The few sites within MZW or RNF tended to have larger differences between the species than most of the regional sites. A pair t-test indicated that the species were significantly different ($p = 0.01$, n = 10, mean difference = 0.4‰), with omission of one outlier sample from the Maroon Bells Wilderness Area for which the $\delta^{34}S$ value for *Xanthoparmelia* (+6.4‰) was much greater than the value for *Usnea* (+5.2‰). Additional paired samples need to be collected to confirm if there is a real difference between the isotope ratios for the species, but these results suggest that there is a potential difference in S uptake between the species in the areas directly downwind of the power stations.

As we have noted, generally we have found heavier S isotope ratios for the lichens in MZW and RNF than for the lichens located more than 100 km from the power stations (Figure 27). There are also distinct isotopic trends for the lichens within the north-south extent of MZW and RNF (Figure 28). The isotope ratios for *Usnea* have a maximum in the southern portion of MZW and the Buffalo Pass to Rabbit Ears Pass area. There is a slight tendency for the *Xanthoparmelia* to have heavier isotopic ratios in these same area, however, it is much less distinct than for the *Usnea*. The heavy isotopic signature of the *Usnea* for the sites in closest proximity and directly downwind of the power stations is similar to the isotopic signature of snowpack, especially for water year 1994, and coal from the region

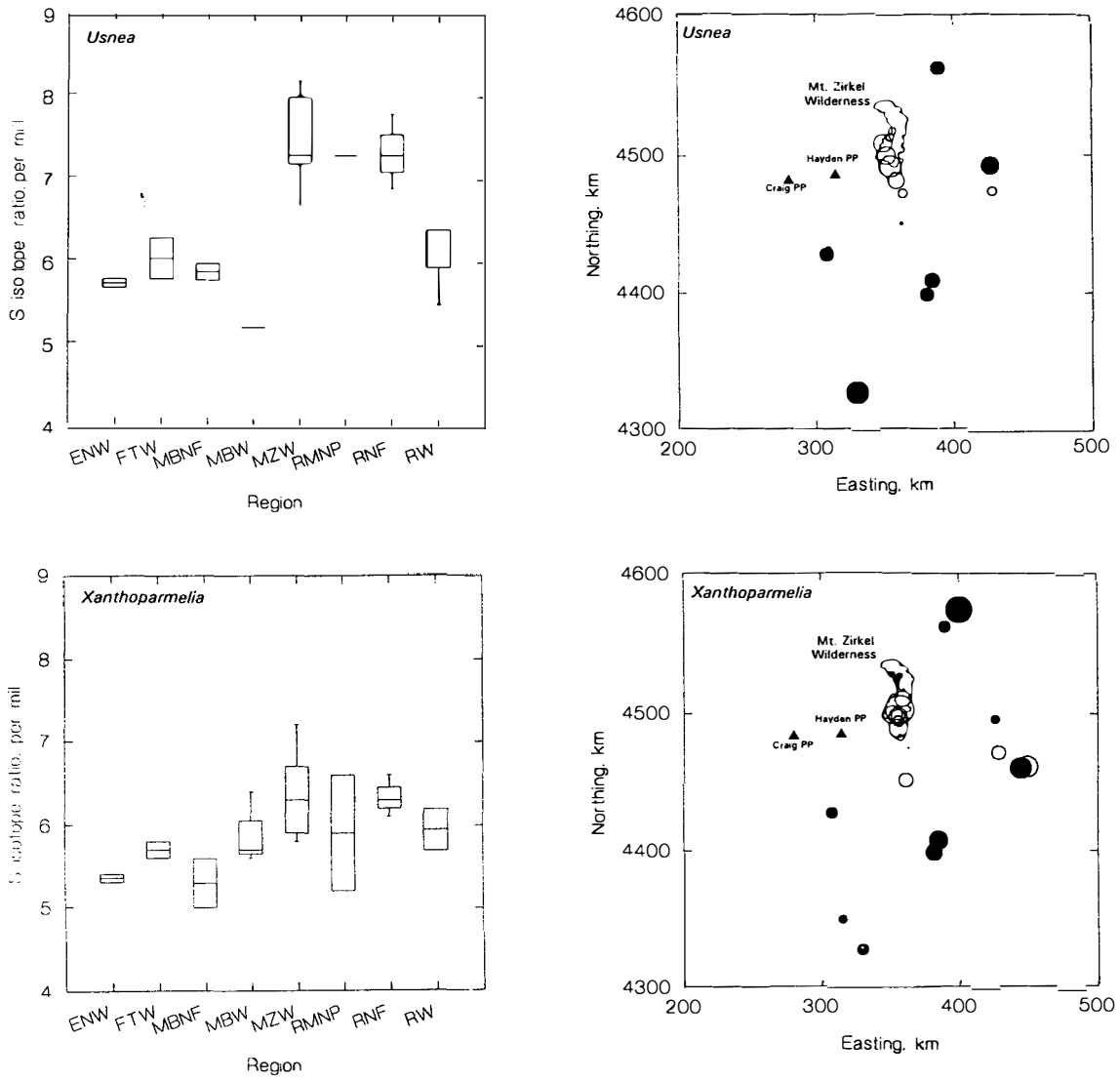

Figure 27. Stable S isotope ratios in *Usnea* and *Xanthoparmelia* by region and location. Stable S isotope ratio distributions are shown as Tukey box plots for each wilderness area and forest unit. Standardized S isotope ratios are plotted versus location as bubble plots with circle diameter proportional to the standardized isotope ratio (mean = 0 and standard deviation = 1). Open-circle diameter increases for isotope ratios heavier than the mean and filled-circle diameter increases for isotope ratios lighter than the mean. Areas: Eagles Nest Wilderness (ENW), Flat Tops Wilderness (FTW), Medicine Bow National Forest (MBNF), Maroon Bells Wilderness (MBW), Mount Zirkel Wilderness (MZW), Rocky Mountain National Park (RMNP), Routt National Forest (RNF), and Rawah Wilderness (RW).

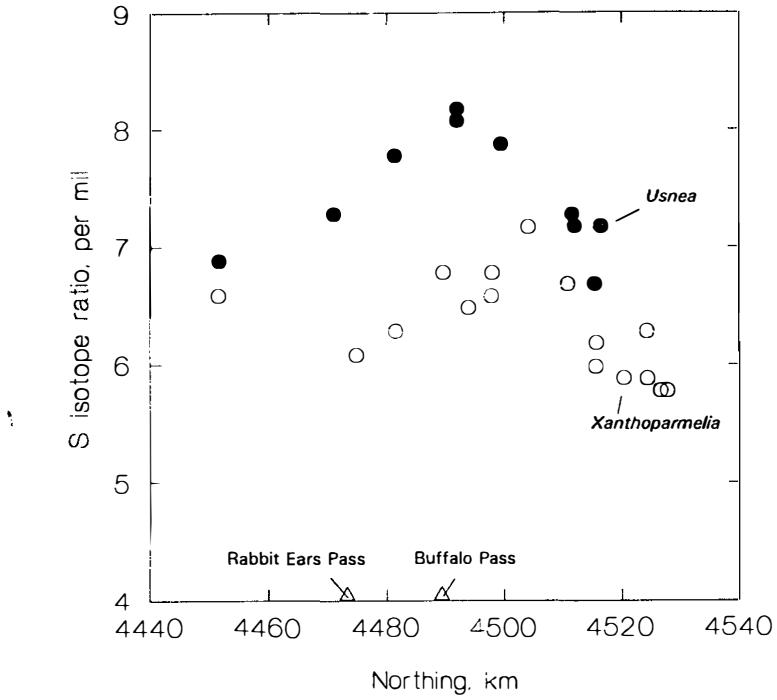

Figure 28. Stable S isotope ratios in *Usnea* and *Xanthoparmelia* versus Northing along the north-south trending traverse in MZW and Routt National Forest. Approximate locations for Buffalo and Rabbit Ears Passes are indicated along the Northing-axis by △.

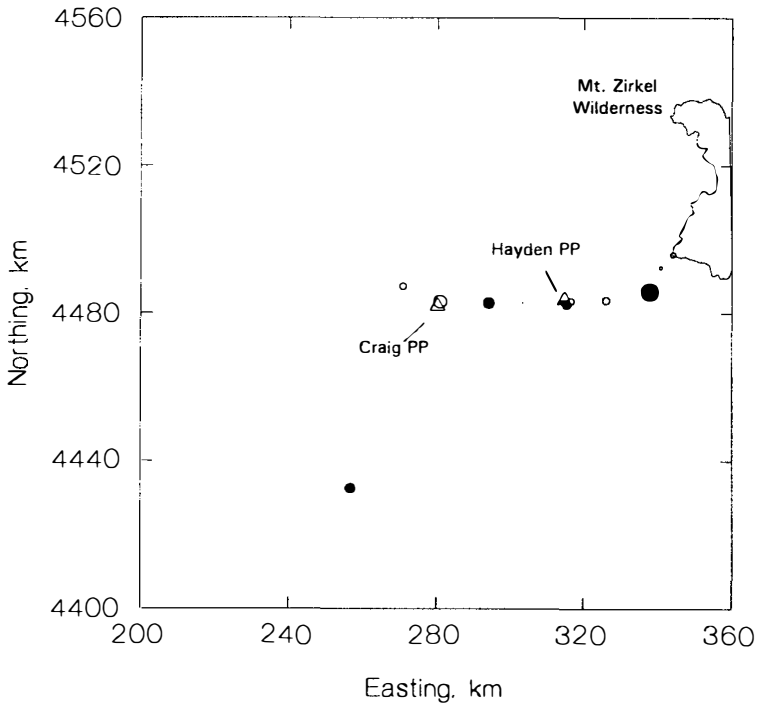

Figure 29. Standardized S isotope ratios in *Tortula* versus Easting in the Yampa Valley. Circle diameter is proportional to the standardized isotope ratio (mean = 0 and standard deviation = 1). Open-circle diameter increases for isotope ratios heavier than the mean and filled-circle diameter increases for isotope ratios lighter than the mean.

suggesting that atmospheric deposition from the local power stations has a strong influence on the lichens within MZW and the southern portion of Routt National Forest.

Within the Yampa Valley the isotopic signature for the moss varied potentially due to confounding natural soil differences along the east-west traverse. The majority of the moss samples had S isotopic ratios of +5 to +7‰, but there are no trends that can be clearly related to emissions from the power stations (Figure 29).

Lead isotopic signatures do not appear to be as promising as an emissions assessment tool for additional research with vegetation in this area, at least in part because of the complexity of geologic environment and the lack of Pb isotopic ratios for emissions. The epiphytic lichens may be a more suitable sample media, however, problems associated with throughfall have been observed to be significant confounders in previous studies (Church, oral communication) and in the very limited test conducted for this study other media were chosen for analysis. The high cost of Pb isotope analyses prohibited additional testing. Sulfur isotope analyses have proved more effective as an assessment tool and we believe that the S isotope results clearly indicate a local S emission source or combination of sources with a heavier isotopic signature than the regional sources of S for lichens sampled in and near MZW. Isotopic signatures for S power station emissions need to be measured directly along with other potential sources of the elements to confirm the source.

Physiological Functions

Photosynthesis, as a membrane bound and pH dependent process, is particularly sensitive to air pollution. Two adverse effects of air pollutants are generally reported from field studies. In Biel, Switzerland, Arb and others (1990) found an increase in chlorophyll concentration in *Parmelia sulcata* which caused a slight increase in photosynthetic activity that they attributed to pollutant effects. At higher pollutant concentrations damage to photosystems has been detected first as a reduction in the rate of photosynthesis and later as an actual breakdown of chlorophyll to phaeophytins (Boonpragob and Nash, 1990b). This type of damage eventually leads to bleaching of lichen tissue and the disappearance of more sensitive species. In MZW, because the power stations have been in operation for a number of years, it is possible that the most sensitive species to the latter type of effects may have already disappeared, although this has not been examined. The lichen species collected in MZW and the Yampa Valley may be insensitive to these types of photosynthetic effects; species or genus differences are not well known. For instance, a species of the genus *Xanthoria* (different than the species collected in the Yampa Valley) has been found to be highly resistant to SO_2 in controlled fumigation studies (Türk and others, 1974) as has been indicated also by its presence in the vicinity of cities (Dalby, 1981).

In this study several measurements for assessing the integrity of photosystems were made: the rate of CO_2 uptake as an indicator of photosynthesis rate; the photometric ratio OD435/OD415 as an indicator of chlorophyll degradation (i.e., a representation of the ratio of chlorophyll concentration to phaeophytin); and chlorophyll content. In addition to these more commonly used methods, chlorophyll fluorescence as an indicator of the photosynthetic capacity or yield (i.e., the fluorescence ratio F_v/F_m) was determined. These latter measurements were done for exploratory purposes and may have suffered from the necessary

collections, shipping, storage, and preconditioning protocol because direct measurements in the field with a portable spectrometer were not possible. It is unclear how these collection parameters may have affected the other photosynthetic measurements, as well.

For samples of *Xanthoparmelia* and *Bryoria* none of the four physiological parameters measured exhibited a significant correlation with precipitation or distance from the Hayden Power Station and only F_v/F_m in *Xanthoparmelia* was significantly different ($p < 0.05$) between MZW and the other regional sites (Figure 30). The difference of F_v/F_m, a measure of stress, was not significant when all sites < 60 km from the Hayden station were compared against sites > 100 km. Although the F_v/F_m ratio may be different, because this fluorescence method has not been field tested it is unclear whether the magnitude of the difference is diagnostic of any pollutant effect.

For the Yampa Valley lichen and moss samples most of the physiological parameters did not have any clear relationship to rainfall or distance from the power stations. However, OD435/OD415 in *Xanthoria* did exhibit a significant inverse relationship to precipitation along the Yampa Valley traverse (Figure 31). Photosynthetic activity as indicated by CO_2 gas exchange was reduced in *Xanthoria* at some sites that were near and to the east of the power stations, especially compared to the western most site. This may be the result of emissions from the power stations. However, local canopy, substrate, topography or other factors may be strongly influencing these measurements and contributing to a large amount of site to site variability as seen for the trace elements.

The physiological parameters measured do not implicate the power stations as having a strong, detectable influence on the lichens sampled outside of the Yampa Valley or the moss sampled within the valley. However, variation in physiological parameters are generally only interpretable when correlated with atmospheric emissions data or element concentrations. Because the parameters measured and their relationship to pollutant impacts have primarily been studied in transplants of sensitive lichen species (Garty and others, 1993; Boonpragob and Nash, 1990b) or in controlled laboratory studies (Sanz and others, 1991), it was of particular interest to examine the parameters in a large field study where the lichens had potential exposure to power station emissions and without the problems associated with transplanting lichens into an area where they did not naturally occur (Werner, 1993). However, laboratory fumigation and transplant studies have less difficulty in minimizing differences in site characteristics that in a large field study such as this one may help obscure potential pollutant effects. The chemical data show clearly that the deposition is elevated and accumulation in the environment is highly probable. It is not clear yet, when these accumulations may reach a threshold level for the lichens to become damaged or for us to detect such damage.

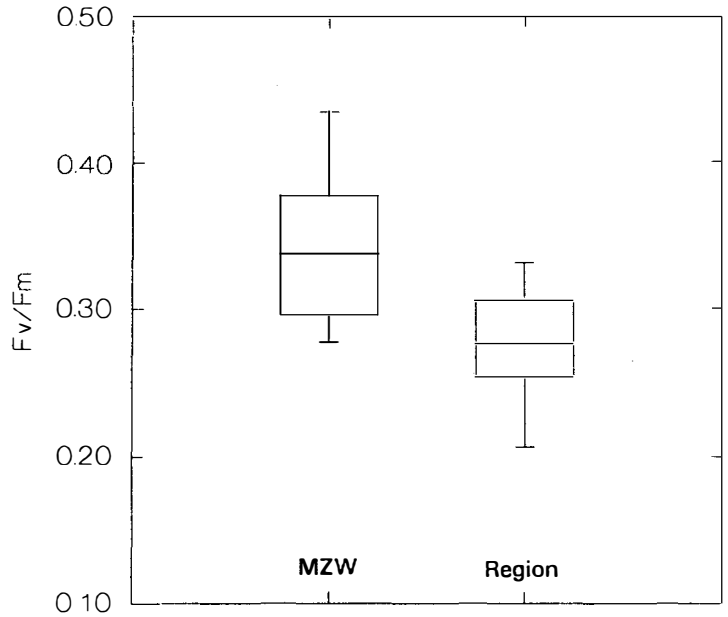

Figure 30. Tukey box plots of the distribution of ratio F_v/F_m in *Xanthoparmelia* MZW and regional sites.

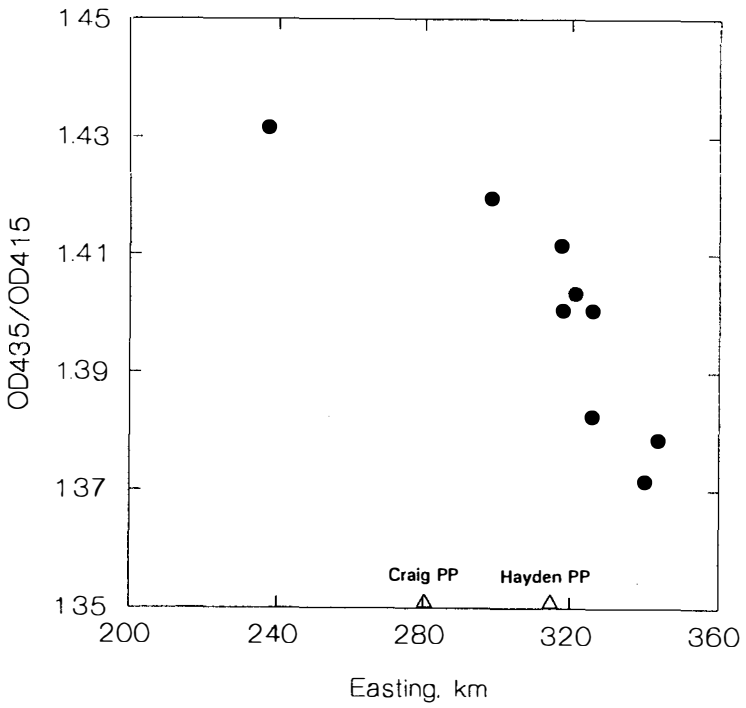

Figure 31. Ratio OD435/OD415 in *Xanthoria* versus Easting in the Yampa Valley. Power station locations are indicated along the Easting-axis by △.

SUMMARY AND CONCLUSIONS

- Major and trace element concentrations and stable S isotope ratios were determined in lichens, *Bryoria*, *Usnea*, and *Xanthoparmelia*, at up to 35 sites in the subalpine zone of MZW and other wilderness and forest lands in NW Colorado. Laboratory error was usually a small proportion of the total element variance. Within MZW most of the variance was attributable to differences among sites and within sites. At regional sites a large proportion of the total variance was also attributable to differences among wilderness areas.

- Nitrogen, S, K, Na, and P concentrations were significantly higher ($p < 0.05$) in *Xanthoparmelia* at sites that were less than 60 km from the Hayden Power Station compared to regional sites more than 100 km away. The group of sites that were within 60 km of the Hayden station was composed primarily of sites within MZW and some sites in Routt National Forest and Flat Tops Wilderness, although the sites in the latter wilderness are largely upwind of the power stations. The data also suggest that Cu, Zn, and S isotope ratios may be higher at the sites closer to the Yampa Valley power stations. Nitrogen, K, and S were also statistically higher in MZW compared to all regional sites, not just the more distant regional sites.

- Stable S isotope ratios in *Usnea* and B concentration in *Bryoria* were significantly higher ($p < 0.05$) at MZW sites and other sites that were less than 60 km from the Hayden Power Station compared to regional sites more than 100 km away. The same results were obtained when only sites in MZW were compared with all regional sites.

- In a prior lichen study with the data reported herein for the first time, based on a limited sampling of *Xanthoparmelia* in the Buffalo Pass area and a few regional sites, higher Hg concentrations were found in the lichens from Routt National Forest sites than at more distant regional sites. Mercury is a volatile element emitted by coal-fired power plants. Although the higher Hg concentrations occur at a location where we have found other potentially coal-combustion related elements to be elevated, these very limited data need further investigation prior to drawing any conclusions related to the source of Hg.

- Exploratory multivariate principal component analysis of the lichen and moss data illustrate the complexity of the interelement relationships in the species and the difficulties in assigning conceptually meaningful labels to suites of elements. The PCA analyses generally show the importance of elements commonly associated with alumino-silicates from eolian material of natural or anthropogenic origin and/or geologic substrates in contributing a large proportion of the variance in the chemical characteristics of the species sampled. Nutrient elements such as N, K, P, and S also play a major role. Spatial plots of PC scores suggest that there may be differences in various suites of elements in MZW compared to regional sites. These differences in

suites of associated elements generally support the single element differences that were observed.

- For the north-south trending sites within MZW and southern Routt National Forest there is a distinct maximum in S isotope ratio in *Usnea* in the vicinity of Buffalo Pass. In the same area there were generally minima for Ca, Mg, Mn, and Sr for both epiphytic lichens. Boron and S also exhibited some concentration differences among the sections of the north-south trending traverse in *Bryoria* and *Usnea*. Among these samples there was moderate correlation of B concentration with precipitation and inverse correlations for Ca, Mn, and Sr with precipitation. Boron is generally elevated in coal-combustion residues compared to the earth's crust. Potentially large amounts of precipitation in the Buffalo to Rabbit Ears Pass area may be contributing to the elevated levels of B and S through increased deposition.

- For *Xanthoparmelia* there were moderately significant differences in Al, B, Be, Li, Na, Ni, Pb, and Zn concentrations and S isotope ratios among the sections of the north-south trending traverse in MZW and southern Routt National Forest. Boron, Be, Li, and S isotope ratios correlated with precipitation along the traverse.

- Within the Yampa Valley, lichen and moss samples exhibited decreasing B concentration trends to the east of the power stations. Aluminum, Fe, and Na also decreased in an eastward direction for the moss, whereas Zn increased for the lichen.

- Lead and S isotope ratios were determined in selected coal samples from the Yampa Valley. Although the coal samples do not represent all of the coal seams that are probably consumed by the power stations and the whole coal may not accurately represent the isotopic signature of emissions (probably most true for Pb), the data provide some reference data for comparison with isotopic ratios in vegetation and precipitation.

- In the very limited testing done, Pb isotope ratios in the coal and vegetation do not provide clear patterns that may be related to any particular source.

- Stable S isotope ratios in the lichen *Usnea* were significantly heavier (average $+7.2 \pm 0.7‰$ for sites < 60 km from Hayden Station, $p < 0.05$) in MZW and nearby sites compared to more distant regional sites (average $+6.0 \pm 0.6‰$ for sites > 100 km from Hayden Station). In the vicinity of Buffalo Pass, the stable sulfur isotope ratio in *Usnea* is heaviest (forming a distinct maximum) for the north-south trending sites within MZW and southern Routt National Forest. These are also the sites that are closest to the power stations and directly downwind. The heavy S isotopic signature found in the *Usnea* tissue in this study corresponds well with the sulfur isotopic ratios found in snow in earlier studies at the same area. The heavy isotope ratios in *Usnea* in MZW and Routt National are consistent with a local sulfur

source with a heavy isotopic signature such as would derive from the combustion of many of the marine-influenced coals in the Yampa Valley.

- Potential impacts on physiological functions of the lichens and moss from power station emissions are not obvious outside of the Yampa River Valley in this study. The chemical data show clearly that the deposition is elevated and accumulation in the environment is highly possible. It is not clear yet, when these accumulations may reach a threshold level for the lichens to become damaged or for us to detect such damage. Local variability in canopy, substrate, topography, lichen age, and a variety of other factors may have obscured any detectable trends for these physiological parameters that have most frequently been tested in controlled laboratory fumigation studies.

- The biogeochemical data suggest that the epiphytic and saxicolous lichens have different properties as atmospheric deposition receptors probably due to differences in growth form, substrate, canopy versus ground sites, and potentially intrinsic chemical properties. Thus, data from all of the lichens must be examined to begin to understand atmospheric deposition influences, but the epiphytic lichens appear to have less confounding influence of eolian dust or substrate contamination.

- In conclusion, the elevated concentration of elements such as N, S, and B (possibly Hg), in lichens in and near MZW and the corresponding heavy stable S isotope ratios in the lichens, snow, and lake water suggest a local atmospheric source that is different in character from the general regional sources as measured at sites distant from MZW. Because we know that the Yampa Valley power stations are the predominant and overwhelming source of N and S emissions in the vicinity and upwind of MZW and speculate, based on limited data, that the S isotopic signature of the power plant emissions is isotopically heavy and similar to that measured in MZW lichens and snow, it is reasonable to assume that the power stations are contributing to atmospheric deposition of S and N and probably some other elements such as B. In addition, it appears that sites in the southern portion of MZW and in Routt National Forest near Buffalo Pass southward to Rabbit Ears Pass that have particularly high precipitation and are closest to the upwind power stations are most likely to be impacted by atmospheric deposition.

- We suggest that additional work with lichens as biomonitors in this area focus on using the epiphytic lichens, measure the chemical characteristics of power station emissions and other potential sources of atmospheric deposition directly and integrated over time. Stable S isotope measurements appear to be the primary key to identifying unique sources. Other isotopic signatures such as Pb or Sr isotope ratios may contribute to source identification, but only if more effort is placed on characterizing multiple sources than was done in this work.

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